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CONTENTS

SEC. A.—PHYSICAL SCIENCES

	Page
Variation with Temperature of the Piezoelectric Effect in Quartz— <i>Arnold Pitt and D. W. R. McKinley</i> - - - -	57
Propagation and Resonance of Composite Waves in Prismatic Rods— <i>R. Rusdy</i> - - - - -	66

SEC. B.—CHEMICAL SCIENCES

Studies on Reactions Relating to Carbohydrates and Polysaccharides. XLVIII. Ethylene Oxide and Related Compounds: Synthesis of the Polyethylene Glycols— <i>Stanley Z. Perry and Harold Hibbert</i> - - - - -	77
The Decomposition of Nitrous Oxide on the Surface of Platinum. II. The Effect of Foreign Gases— <i>E. W. R. Steacie and J. W. McCubbin</i> - - - - -	84
The Polarization of Liquids and their Saturated Vapors in the Critical Temperature Region— <i>J. Marsden and O. Maass</i> -	90
The Liquid Densities of Propylene and Methyl Ether as Determined by a Modified Dilatometer Method— <i>D. B. Pall and O. Maass</i> - - - - -	96
The Sorption of Iodine by Polyvinyl Alcohol— <i>Wilfred Gallay</i> -	105

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VARIATION WITH TEMPERATURE OF THE PIEZOELECTRIC EFFECT IN QUARTZ¹

BY ARNOLD PITT² AND D. W. R. MCKINLEY³

Abstract

As a result of some previous experiments there were indications that the elastic vibrations set up in quartz showed an anomalous property at the temperature of liquid helium. In order to decide this point, experiments were carried out on the piezoelectric activity of quartz at progressively lower temperatures until that of liquid helium was reached. Although a decrease in this activity of only 1% had been observed by others working over the range from room temperature to liquid hydrogen temperatures, the present experiments show a total decrease of 12% at the temperature of liquid helium. Two methods were used, a statical method employed where the temperature could be held constant, and a dynamical method to ascertain the temperature at which any marked change in activity would just become evident. Results by the dynamical method indicate that a sudden decrease in activity occurs at about 5° K. In addition, the dynamical method was extended to higher temperatures, so as to include in this paper values of the piezoelectric activity of quartz from 4° K. to 813° K.

Introduction

In order to measure ultrasonic wave velocities in liquid oxygen, hydrogen and helium, Pitt and Jackson used as a source a vibrating quartz plate. While very satisfactory results were obtained for liquid oxygen and liquid hydrogen, it was found impossible to obtain satisfactory measurements in liquid helium. It was thought that at the temperature of liquid helium the amplitude of oscillation of the quartz plate was reduced, and in order to test this point it was decided to measure the piezoelectric effect in quartz as the temperature was decreased to the boiling point of liquid helium.

Quartz forms a hexagonal crystal terminating in corresponding pyramids. The line joining the vertices of the two pyramids is an axis of symmetry, called the optic axis. The symmetry is trigonal so that three axes may be taken in the crystal; the *X*, or electric, axis passing through opposite edges; the *Y*, or mechanical, axis passing through opposite faces; and both *X* and *Y* being mutually perpendicular to the *Z*, or optic axis.

If a rectangular block of quartz with sides cut parallel to the three axes of the crystal be compressed along the *X*-axis it develops a charge according to the equation:—

$$Q = H.F_z, \quad (1)$$

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where Q is the quantity of charge, F_x the force in the X -direction, and H the piezoelectric constant.

If it be strained along the Y -axis the charge appears according to the equation:—

$$Q = H.F_y \cdot \frac{L_y}{L_x}, \quad (2)$$

where L_x and L_y are the corresponding linear dimensions.

Methods of Measuring Piezoelectric Effect

It may be pointed out that the piezoelectric activity may be measured statically or dynamically. The statical methods, corresponding to Equations (1) and (2) above, consist in applying a steady mechanical force to the quartz plate and measuring the charge produced. By suitable variations of the dimensions, much larger charges can be obtained by the method represented by Equation (2). However, practical difficulties led to the adoption of the simpler method of Equation (1) for the experiments at low temperatures.

In the dynamical methods an alternating e.m.f. is applied to the faces of the quartz plate, which then vibrates mechanically at this frequency. The frequency of the applied e.m.f. is usually adjusted to a natural vibration frequency of the plate, under which condition the amplitude of vibration is greatly increased. Any change in crystal activity may be observed by reaction effects in the generator circuit supplying the e.m.f.

As quartz approaches the critical temperature of 576°C. and changes from α - to β -quartz, its physical properties show anomalous variations, and marked discontinuities occur at this critical temperature. Perrier (5) found that, starting at room temperature, the piezoelectric effect was independent of temperature up to 200°C. , above which it decreased rapidly and disappeared at 579°C. ; it reappeared on cooling at 576°C. Dawson (1) also found this decrease and observed a lag in the effect as the crystal cooled. Schulwas-Sorokina (7) pointed out that the statical methods failed to take account of the electrical conductivity of quartz, which increases exponentially with temperature, and that a dynamical method should be used at higher temperatures. However, as the question of the relative reliability of the statical and dynamical methods does not arise at low temperatures, it was decided to use the statical method for this region.

Apparatus—Statical Method

After some preliminary experiments in statical methods, the apparatus in Fig. 1 was designed so as to fit into the flask containing the liquid helium. The quartz plate was supported in a cup near the bottom of the flask, and the pressure was applied by a weight on a platform at the top of the apparatus, connection between the platform and the plate being made by a rod which pressed on a point on the top of the plate. The pressure rod was made of German silver 0.6 cm. in diameter, and the upper part of the apparatus was supported by means of a German silver tube 1.2 cm. in diameter. Small

holes were drilled in the cup containing the plate in order to allow free passage of the liquid helium around the plate. Since the weight had to be applied externally, the supporting rod had to be free-moving; in order to carry this out a soft rubber diaphragm was clamped to an ebonite locknut. Ebonite insulation was used throughout and the charge was taken from the point at which the pressure rod touched the crystal. Electrical connections from this rod to an electrometer are indicated in the diagram.

Six specimens of quartz, cut in the form of discs and parallelepipeds and free from twinning, were carefully tested at room temperature for consistency of observations, since other workers have found individual specimens to vary considerably in piezoelectric activity over the surface of the crystal. The piece finally selected was a rectangular block of dimensions, 13.0 mm. along X, 17.2 mm. along Y, and 22.0 mm. along Z.

The weight of 3700 gm. was lifted a short distance from the plunger platform by a rope-and-pulley arrangement, observations being made after the weight was lifted. The charge was measured by means of a standard quadrant electrometer connected to the plunger, with the crystal in air at room temperature, in liquid air, and in liquid helium. The change in capacity of the system as a whole was negligible when the crystal was immersed in liquid helium.

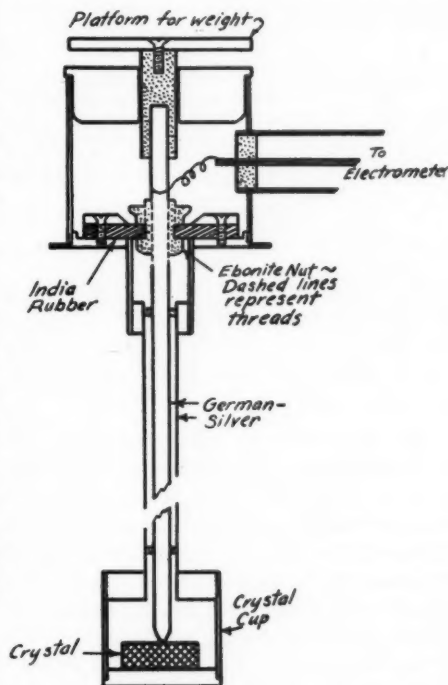


FIG. 1. Apparatus used in the static method at low temperatures.

Results with Static Method

The following results were obtained.

TABLE I
VARIATION OF PIEZOELECTRIC EFFECT WITH TEMPERATURE

Temperature, °K.	Electrometer deflections, mm.	Decrease from reading at 296° K., %
296	84.6 ± 0.3 (mean of 5 sets of 15 to 21 readings each)	—
83	83.5 ± 0.4 (2 sets of 12 each)	1.3
4.2	74.4 ± 0.4 (1 set of 17 readings)	12.0

Some time later the experiment was repeated at room temperature and at liquid helium temperature. The results are given in Table II.

TABLE II
VARIATION OF PIEZOELECTRIC EFFECT WITH TEMPERATURE

Temperature, °K.	Electrometer deflections, mm.	Decrease from reading at 296° K., %
296	65.7 ± 0.2 (mean of 4 sets of 16 readings each)	—
4.2	57.5 ± 0.2 (mean of 22 readings)	(12.4 \pm 0.7)

The decrease of about 1.3% at 83° K. (liquid air temperature) agrees with the work of Omnes and Beckman (5), who observed no further definite decrease between 80° K. and 20° K. The decrease of 12% found above seems unexpected since the modulus of elasticity of quartz increases slightly at lower temperatures.

To determine the temperature at which this drop in the piezoelectric activity occurs, it would be necessary to hold the temperature stationary at various points between the temperatures of liquid hydrogen and liquid helium. This could not be done in the side flask of the liquefier in which the above-mentioned experiments were carried out, and therefore a dynamical method was developed in order to permit testing the crystal activity under known temperature conditions, and without the necessity for external mechanical adjustment such as the statical method required.

Apparatus for Dynamical Methods, and Results

The quartz plate used was 24 mm. square and 0.81 mm. thick with the electric axis perpendicular to the plane parallel faces. Dye (2) and Cady have used a similar plate as a resonator to determine the equivalent electrical constants of a vibrating quartz plate, and so obtain the piezoelectric constant by calculations from these quantities. Their methods necessitate the use of several tuned circuits, and since the frequency of the natural resonant vibration of the quartz plate changes rapidly with temperature, it is difficult to keep the circuits tuned to the quartz frequency without altering those electrical quantities which are used to calculate the piezoelectric activity.

As a second method, the quartz plate might be used as an oscillator in the grid circuit of a vacuum tube. Any change in the crystal activity would cause a variation in anode current, or more especially a variation in the radio-frequency current in the plate circuit. However, this circuit was not adopted, because the resonance curve is unsymmetrical and depends on whether resonance is approached from the low or high frequency side, making it difficult to reproduce conditions as the temperature varies.

The usual crystal oscillator was therefore discarded in favor of a circuit developed by Lamb (3), and shown in Fig. 2. The load circuit of the crystal is L_1C_1 placed, in effect, in the screen-grid circuit. That is, the cathode, control-grid and screen-grid act as a triode whose output is internally coupled to a tetrode consisting of the same three elements plus the plate. If another

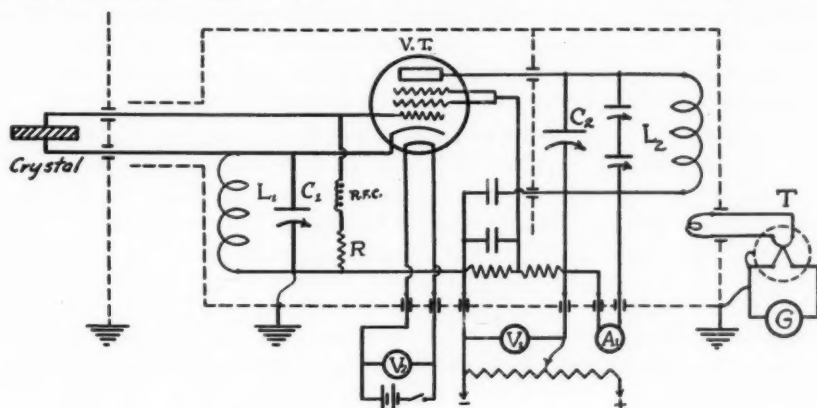


FIG. 2. Oscillator circuit used in the dynamical method at high and low temperatures.

circuit L_2C_2 be placed in the plate lead it may be tuned to resonance with the crystal frequency, an advantage as the resonance curve is then symmetrical since the crystal does not cease to oscillate. L_2C_2 may be tuned to the second, third, etc. up to the sixth or seventh harmonic of the crystal with measurable outputs. The reaction on the crystal circuit as L_2C_2 is tuned through an harmonic frequency is negligible: an almost imperceptible drop in plate current takes place when resonance has been reached. A peculiarity of such an oscillator is that the circuit L_1C_1 may be tuned over a range from the fundamental of the crystal to its second harmonic and still permit the crystal to oscillate. The plate current curve for variation of L_1C_1 is smooth and climbs slowly from its lowest point at resonance, which in this case was 3540 kc. to its out-of-oscillation value reached at about 7500 kc. Hence if L_1C_1 be set at about 4500 to 5000 kc. the crystal frequency may change without causing more than slight variations in the radio-frequency output. Measurement of the radio-frequency output in L_2C_2 when tuned to an harmonic is a very sensitive indication of any variation in crystal activity, since a slight change in grid bias of a tube acting as a frequency multiplier will cause a large variation in harmonic output, and the bias is here obtained from the rectified current through R , this current being a function of crystal activity under given electrical conditions.

A single turn aperiodic loop was loosely coupled to L_2C_2 and connected to a heater type thermocouple and galvanometer G . The filament and plate voltages were applied for an hour before taking readings of G . The crystal

was platinized (for use in a later experiment particularly) and supported in a small open holder inside the helium flask. Leads of approximately five feet were necessary to connect it to the oscillator, but these had no observable disturbing effect.

The crystal was cooled to liquid air temperature and held there while readings were made, then cooled directly to 14° K. and from this temperature down, the helium pressure gave an accurate measure of temperature. The temperature had to be held constant for 10 min. at each reading to enable the crystal to cool throughout; otherwise operation was unsteady.

No change in activity was observed from 14° K. to about 5.5° K. Between 5.5° K. and the boiling point of helium (4.2° K.) the activity decreased suddenly by about 10%. No further decrease was observed as the temperature was lowered with the crystal in helium gas at very low pressure. This indicated that possible damping of the crystal due to the dense helium gas near 4.2° K. was negligible, and that the decrease was due to a change in piezoelectric activity. In this dynamic method the liquid helium was not permitted to cover the crystal. The experiment was repeated later at temperatures decreasing to 5° K. when the sudden decrease in output was again observed.

The elasticity of the crystal becomes more perfect as the temperature is lowered and hence an increase in output might be expected. At liquid air temperature a slight increase was observed, with the dynamic method, and, though the piezoelectric effect had decreased slightly, (*cf.* previous statical experiment), the increased elasticity apparently masks the decrease at this temperature. However, a sharp decrease in output occurred between 5.5° K. and 4° K., so it would seem that a correspondingly greater decrease in the piezoelectric activity must occur to account for this drop.

Dynamical Method at High Temperature

As has been mentioned, the statical methods of measuring the piezoelectric effect in quartz fail at high temperatures owing to the increasing electrical conductivity, so the dynamical method described above was applied in the range from room temperature up to 576° C.

To avoid using separate metal electrodes, the two crystal faces were sputtered with platinum and the crystal supported vertically on edge on a small mica platform by means of two light platinum springs pressing at the centres of the faces. The platform was held by bars of German silver which also served as leads, and the crystal assembly, complete with heat shield and platinum-platinum-rhodium thermocouple, could be slid into a small electric oven. The thermocouple was connected to a typical potentiometer circuit; the sensitivity was better than 0.5° at 600° C. It was found that the crystal had to be heated very slowly to avoid setting up mechanical stresses which greatly affected the output. For this reason the oven temperature was held stationary within 0.5° for 10 min. before each reading was taken; this time was sufficient

to eliminate possible pyro-electric effects. As readings were made at temperatures about 15 degrees apart, the time taken to raise the crystal to 540° C. was about seven hours.

For the first run, in which a generator plate potential of 150 volts was used, the relation between radio-frequency output and temperature is shown in Fig. 3. The crystal ceased oscillating at 532° C. and re-started at 528° C.

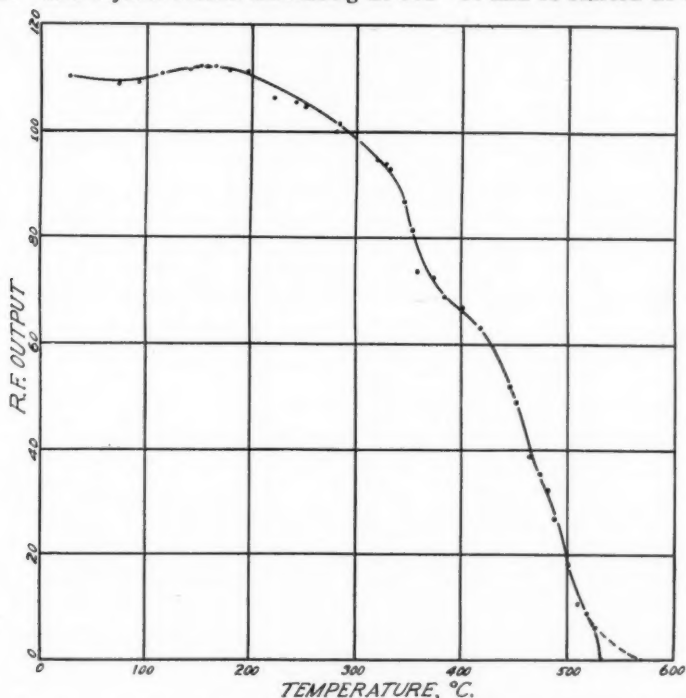


FIG. 3. Curve showing variation of radio-frequency output with temperature in the first run, crystal being slowly heated.

again ceasing at 532° C. Then the temperature was slowly lowered in the same manner as it had been raised, and the readings were found to correspond point for point. It was observed that on sudden cooling a higher output was momentarily maintained than was normal for that observed temperature, the output becoming normal as the crystal became uniformly cooled. When the crystal finally reached room temperature the output was identical with that at the start of the experiment, indicating that there is no lag of the order of several hours in the piezoelectric activity, in contradiction to Dawson's (1) statical results, though the curve for rising temperature is of the same form as that given by him.

The experiment was repeated with a generator plate potential of 250 volts and with L_1C_1 set to give a slightly different operating point on the L_1C_1

resonance curve. The results of this run for rising temperatures are shown in Fig. 4, solid curve, which is of the same form as that of the previous run, except for small variations. The point at which the crystal ceased oscillating was now 540°C . Lowering the plate voltage to 150 volts as before, this point

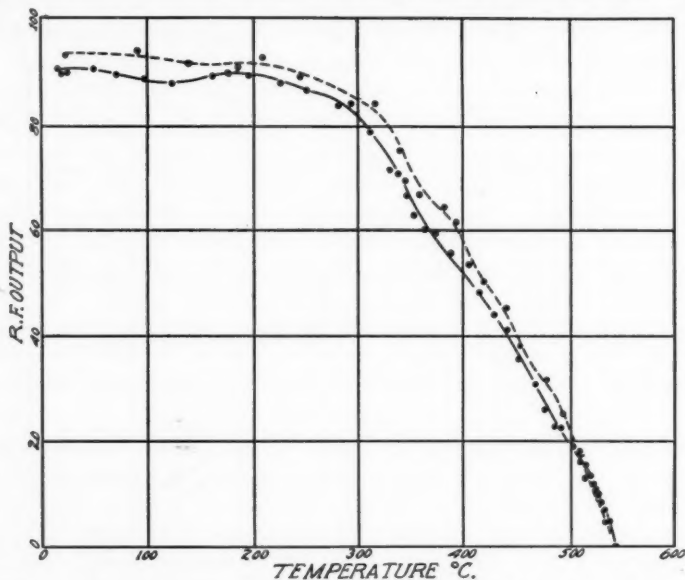


FIG. 4. Curve showing variation of radio-frequency output with temperature in the second run. Solid curve—crystal being slowly heated; broken curve—crystal being rapidly cooled.

dropped to 532°C ., its former value, and increasing voltage to 250 volts brought it back again to 540°C ., indicating that it might be possible in a limiting case to approach the critical temperature of 576°C .

Now, starting at 540°C . the crystal was *rapidly* cooled and readings were made. The points obtained are more erratic than those on the curve for the slowly cooling crystal, but lie well *above* the heating curve. When the temperature was that of the room the value of the output was 3% higher than at the start, but it dropped down to the initial value in about six minutes and remained there. The curve for rapid cooling is shown dotted in Fig. 4. Presumably the crystal surfaces contract first on rapid cooling, producing a mechanical clamping and increasing the output momentarily. As has been mentioned, the reverse action took place on sudden heating and the crystal had to be held at a given temperature for several minutes before the output reached a maximum steady value.

A third run was made with a plate voltage of 200 and still another value of L_1C_1 . The outputs shown by the three curves were multiplied by suitable correction factors to equalize their values at room temperature and the three curves were then superposed; they showed but slight deviations from a mean

curve, which is given in Fig. 5. Temperatures are plotted on a centigrade scale and output readings of G are plotted on an arbitrary scale. The small dotted portion indicates the probable curve up to the critical temperature, if the crystal would oscillate over this range.

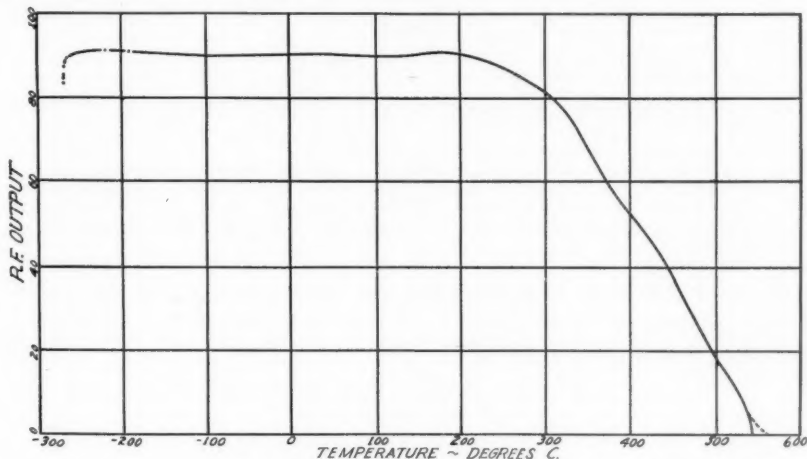


FIG. 5. Mean curve showing variation of radio-frequency output (crystal activity) with temperature from -269° to 576° C. Broken line indicates probable curve up to the critical temperature. The apparent broken line at the low temperature end of the curve is due to points representing actual readings.

Although the piezoelectric activity is connected with the radio-frequency output readings, as previously mentioned, the exact relation is not known. The significance of the curve of Fig. 5 is therefore qualitative, being used to determine the temperature at which a change occurs, rather than the absolute value of the change.

The results from the low temperature work with the oscillating quartz crystal have been included in Fig. 5, showing the sudden decrease at about 5° K., and giving a complete graph representation of its activity from 4° K. to 813° K.

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PROPAGATION AND RESONANCE OF COMPOSITE WAVES IN PRISMATIC RODS¹

By R. RUEDY²

Abstract

By taking into account the three main terms of the equation of motion of the prismatic rod, there is obtained for the frequency a cubic equation which is in good agreement with the experimental results when the thickness of the rod is not negligible compared with its length but does not exceed about one-fifth of the length. It corresponds to the equation obtained for a system with three degrees of freedom.

For a composite vibration consisting of a wave of dilatation and a wave of distortion in the direction of the smallest dimension of the rod, and waves of dilatation in the two other directions, the equations of motion combined with some of the boundary conditions yield another cubic equation for the resonance frequencies.

Fulfillment of Both Groups of Boundary Conditions

The equations of motion applying to the vibrations in a solid body are satisfied by expressions such as

$$\begin{aligned}u &= A_1 \sin \alpha x \cos \beta y \cos \gamma z \\v &= A_2 \cos \alpha x \sin \beta y \cos \gamma z \\w &= A_3 \cos \alpha x \cos \beta y \sin \gamma z,\end{aligned}$$

providing that the angular frequency p , and the constants α , β , γ , inversely proportional to the wave-length, are connected by the following relation

$$\left(\frac{f}{F}\right)^6 - 2\left(\frac{f}{F}\right)^4 \frac{2-3\sigma}{1-2\sigma} + \left(\frac{f}{F}\right)^2 \frac{5-6\sigma}{1-2\sigma} - \frac{2(1-\sigma)}{1-2\sigma} = 0,$$

with

$$F^2 = \frac{1}{2(1+\sigma)} (f_1^2 + f_2^2 + f_3^2),$$

where f_1 , f_2 and f_3 are arbitrary frequencies. This equation has, in general, two equal roots, namely, $f/F=1$, while the third root is equal to $2(1-\sigma)/(1-2\sigma)$. In other words, when the body vibrates freely, the waves formed are either pure waves of distortion, or pure waves of dilatation. In order to satisfy all the boundary conditions of one group, for instance, to ensure absence of shearing stress at the surface of the prismatic bar, it is necessary to limit f_1 , f_2 and f_3 to the longitudinal resonance frequencies of the rod. The second group of boundary conditions ensuring absence of normal pressures is not as a rule accurately satisfied at the same time, so that alternating forces remain at the surface of the rod and produce additional vibrations in the rod or in the surroundings. The complete solution may, therefore, be expected to contain two or more waves existing side by side at a frequency which differs from the resonance frequency, or it must consist of a wave of more complicated structure having a frequency which differs from that of pure waves of vibration or distortion.

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Ordinary Longitudinal Waves

The required wave of composite structure may be deduced by writing the equations of motion in the following form

$$\rho \frac{\partial^2 u}{\partial t^2} = (\lambda + 2G) \frac{\partial^2 u}{\partial x^2} + G \left(\frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} \right) + (\lambda + G) \frac{\partial}{\partial x} \left(\frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} \right) = E \frac{\partial^2 u}{\partial x^2} + \sigma E \left(\frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} \right) + \frac{2\sigma^2 E}{(1+\sigma)(1-2\sigma)} \frac{\partial^2 u}{\partial x^2} + \frac{E(1-2\sigma-2\sigma^2)}{2(1+\sigma)} \left(\frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} \right) + \frac{E}{2(1+\sigma)(1-2\sigma)} \frac{\partial}{\partial x} \left(\frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} \right),$$

where $G = \frac{E}{2(1+\sigma)}$, is the modulus of rigidity or shearing elasticity,

$$\lambda = \frac{E\sigma}{(1+\sigma)(1-2\sigma)}, \text{ is an elastic constant,}$$

with similar equations for v and w . Written in this way the equation shows the influence of E , Young's modulus of elasticity, and σ , Poisson's ratio. From the work with very thin long rods it is known that longitudinal waves are sufficiently well described by the first term on the right-hand side of the equation, so that all the other terms must be very small, or cancel one another. It is probable that the last term is always negligible so long as no nodes are formed within the smaller cross section of the rod. A more accurate result may be obtained by considering, first the equation

$$\frac{\partial^2 u}{\partial t^2} = c_o^2 \frac{\partial^2 u}{\partial x^2} + \sigma c_o^2 \left(\frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} \right)$$

in which $c_o^2 = E/\rho$, and then the equation

$$\frac{\partial^2 u}{\partial t^2} = \frac{1-\sigma}{(1+\sigma)(1-2\sigma)} c_o^2 \frac{\partial^2 u}{\partial x^2} + \frac{1}{2(1+\sigma)} c_o^2 \left(\frac{\partial^2 u}{\partial y^2} + \frac{\partial^2 u}{\partial z^2} \right).$$

In both cases the solutions

$$\begin{aligned} u &= A_1 \sin \alpha x \cos by \cos cz e^{i p t} \\ v &= A_2 \cos \alpha x \sin \beta y \cos cz e^{i p t} \\ w &= A_3 \cos \alpha x \cos by \sin \gamma z e^{i p t} \end{aligned}$$

or a sum of similar expressions may be retained as approximations. Then

$$p^2 = \alpha^2 c_o^2 + \sigma c_o^2 b^2 + \sigma c_o^2 c^2$$

For very thin and long rods p^2 is nearly equal to zero, and the equation may be satisfied by putting $c_o^2 b^2$ and $c_o^2 c^2$ equal to p^2 . Using frequency in place of angular frequency

$$f^2 = f_1^2 + \sigma f^2 + \sigma f^2$$

with similar equations for v and w . The "determinant" of the three equations furnishes the equation for the frequency

$$f^6 - (f_1^2 + f_2^2 + f_3^2) \frac{(1-\sigma)}{(1+\sigma)(1-2\sigma)} f^4 + \frac{f_1^2 f_2^2 + f_2^2 f_3^2 + f_3^2 f_1^2}{(1+\sigma)^2 (1-2\sigma)} f^2 - \frac{f_1^2 f_2^2 f_3^2}{(1+\sigma)^2 (1-2\sigma)} = 0,$$

an equation which is in very good agreement with measurements obtained with rods when f_1 , f_2 and f_3 are the three longitudinal frequencies of the rod, f_1 being about ten times f_2 , and f_2 about equal to f_3 . The departure from whole numbers which the overtones show as the diameter of the rod is

increased appears clearly in Table I, which gives the first ten resonance frequencies measured in multiples of the fundamental frequency. The order of magnitude of this deviation may be quickly gauged by using the following relation which holds for the roots f_I , f_{II} and f_{III} of the cubic equation

$$\frac{1}{f_I^3} + \frac{1}{f_{II}^3} + \frac{1}{f_{III}^3} = \frac{1}{f_1^3} + \frac{1}{f_2^3} + \frac{1}{f_3^3}$$

TABLE I

DEPARTURE OF HARMONICS OF A VIBRATING PRISMATIC ROD FROM WHOLE NUMBERS n
FOR $\sigma=0.3$

$f_1 : f_2 : f_3$	$n = 1$	2	3	4	5	6	7	8	9	10
1 : 20 : 20	1	2	3	4	5	6	7	7.9	8.8	9.7
1 : 10 : 20	1	2	3	4	4.9	5.8	6.7	7.6	8.3	8.7
1 : 10 : 10	1	2	3	3.9	4.9	5.8	6.6	7.4	8.2	8.7
1 : 5 : 10						4.4			8.6	

The equation obtained for the frequency agrees with the equation which is valid for a vibrating system with three degrees of freedom, with coupling by inertia, as if each layer of the rod were equivalent to such a system.

The experimental results available at present do not call for a further refinement of the theory for thicker rods.

Composite Waves

A different type of solution which comes nearer to fulfilling the boundary conditions may be obtained by assuming that the resulting vibration consists of a wave of dilatation and a wave of distortion, as when, for instance,

$$\begin{aligned} u &= u_1 + u_2 = (\alpha e^{i\gamma z} + A_1 e^{ihz}) \sin(\alpha x + \beta y) e^{ipt} \\ v &= v_1 + v_2 = (\beta e^{i\gamma z} + A_2 e^{ihz}) \sin(\alpha x + \beta y) e^{ipt} \\ w &= w_1 + w_2 = (-i\gamma e^{i\gamma z} + A_3 e^{ihz}) \cos(\alpha x + \beta y) e^{ipt} \end{aligned}$$

The constants are so chosen that the first term takes into account the change in volume, and satisfies the condition for absence of rotation, while at the same time according to the equations of motion

$$p^2 = c_1^2 (\alpha^2 + \beta^2 + \gamma^2) .$$

The second term of the sum obeys the equation for the wave of distortion

$$\nabla u_2 + \frac{p^2}{c_2^2} u_2 = 0 \quad \nabla v_2 + \frac{p^2}{c_2^2} v_2 = 0 \quad \nabla w_2 + \frac{p^2}{c_2^2} w_2 = 0 ,$$

where

$$c_1^2 = \frac{E(1-\sigma)}{\rho(1+\sigma)(1-2\sigma)} \quad c_2^2 = \frac{E}{2\rho(1+\sigma)} ,$$

providing that the volume change $\partial u_2/\partial x + \partial v_2/\partial y + \partial w_2/\partial z$ vanishes, or that

$$\alpha A_1 + \beta A_2 + ih A_3 = 0 ,$$

and

$$p^2 = c_2^2 (\alpha^2 + \beta^2 + h^2) .$$

The equations of motion alone restrict, therefore, to a certain extent the choice in the frequency, and cause it to depend on the amplitude of the components of the wave of distortion.

The three conditions

$$\begin{aligned}\alpha A_1 + \beta A_2 + ihA_3 &= 0 \\ p^2 &= c_1^2(\alpha^2 + \beta^2 + \gamma^2) = c_2^2(\alpha^2 + \beta^2 + h^2)\end{aligned}$$

have to be fulfilled at the same time. The more nearly σ approaches $1/2$, that is, the more nearly incompressible, or jelly-like, the material from which the rod is made, the larger is the value of h required in order to satisfy the second equation for a given choice of α , β and p . At the other extreme, for σ nearly zero, the value of h^2 is equal to $\alpha^2 + \beta^2 + 2\gamma^2$. In the case of an infinite solid

$$\alpha^2 + \beta^2 - \frac{2(1-\sigma)}{1-2\sigma}(\alpha^2 + \beta^2 + \gamma^2) = h^2.$$

For the normal stresses, when

$$\begin{aligned}e &= \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} \\ X_x &= \lambda e + 2G \frac{\partial u}{\partial x} = \left(\lambda \frac{p^2}{c_1^2} \epsilon^{i\gamma z} + 2G\alpha^2 \epsilon^{i\gamma z} + 2\alpha G A_1 \epsilon^{ihz} \right) \cos(\alpha x + \beta y) \\ Y_y &= \lambda e + 2G \frac{\partial v}{\partial y} = \left(\lambda \frac{p^2}{c_1^2} \epsilon^{i\gamma z} + 2G\beta^2 \epsilon^{i\gamma z} + 2\beta G A_2 \epsilon^{ihz} \right) \cos(\alpha x + \beta y) \\ Z_z &= \lambda e + 2G \frac{\partial w}{\partial z} = \left(\lambda \frac{p^2}{c_1^2} \epsilon^{i\gamma z} + 2G\gamma^2 \epsilon^{i\gamma z} + 2ihGA_3 \epsilon^{ihz} \right) \cos(\alpha x + \beta y)\end{aligned}$$

For the shearing strains

$$\begin{aligned}X_y = Y_x &= (2\alpha\beta \epsilon^{i\gamma z} + \beta A_1 \epsilon^{ihz} + \alpha A_2 \epsilon^{ihz}) \cos(\alpha x + \beta y) \\ X_z = Z_x &= (2i\alpha\gamma \epsilon^{i\gamma z} + ihA_1 \epsilon^{ihz} - \alpha A_3 \epsilon^{ihz}) \sin(\alpha x + \beta y) \\ Y_z = Z_y &= (2i\beta\gamma \epsilon^{i\gamma z} + ihA_2 \epsilon^{ihz} - \beta A_3 \epsilon^{ihz}) \sin(\alpha x + \beta y)\end{aligned}$$

These stresses over the boundary surfaces should vanish unless external forces act upon the surface, or the surface exerts a force upon the surroundings. It is not possible to satisfy all the boundary conditions at the same time, but if in the case of a flat rod the stresses disappear at the two parallel surfaces of largest area, supposed to be normal to the z -axis, the remaining conditions may be neglected without appreciably changing the result.

In order that the stresses X_z and Y_z will disappear at $z=0$ it is necessary to have

$$\begin{aligned}2i\alpha\gamma + ihA_1 - \alpha A_3 &= 0 \\ 2i\beta\gamma + ihA_2 - \beta A_3 &= 0,\end{aligned}$$

or since

$$\alpha A_1 + \beta A_2 + ihA_3 = 0$$

it follows that

$$\begin{aligned}\frac{A_1}{A_2} &= \frac{\alpha}{\beta} \\ A_1 &= \frac{2\alpha\gamma h}{\alpha^2 + \beta^2 - h^2} \quad A_2 = \frac{2\beta\gamma h}{\alpha^2 + \beta^2 - h^2} \quad A_3 = \frac{2i\gamma(\alpha^2 + \beta^2)}{\alpha^2 + \beta^2 - h^2}\end{aligned}$$

These coefficients are very small when the value of h is large; they do not affect the choice of α , β , γ and h .

In order that Z_z will disappear at $z=0$ it is necessary to have

$$\lambda \frac{p^2}{c_1^2} + 2G\gamma^2 + 2iGhA_3 = 0$$

or, since

$$\frac{p^2}{c_2^2} - 2(\alpha^2 + \beta^2) + 2ihA_3 = 0,$$

$$\frac{p^2}{c_2^2} - 2(\alpha^2 + \beta^2) = \frac{4\gamma h(\alpha^2 + \beta^2)}{\alpha^2 + \beta^2 - h^2}$$

$$\left(2(\alpha^2 + \beta^2) - \frac{p^2}{c_2^2}\right)^4 = (\alpha^2 + \beta^2)^4 \left(2 - \frac{p^2}{c_2^2(\alpha^2 + \beta^2)}\right)^4 = 16(\alpha^2 + \beta^2)^4 \left(1 - \frac{p^2}{c_1^2(\alpha^2 + \beta^2)}\right) \left(1 - \frac{p^2}{c_2^2(\alpha^2 + \beta^2)}\right).$$

On rearranging and on dividing by p^2 , the expression

$$p^6 - 8p^4 c_2^2 (\alpha^2 + \beta^2) + 8p^2 c_2^4 (\alpha^2 + \beta^2)^2 \left(3 - 2 \frac{c_2^2}{c_1^2}\right) - 16c_2^6 (\alpha^2 + \beta^2)^3 \left(1 - \frac{c_2^2}{c_1^2}\right) = 0$$

is obtained as the equation for the frequency. It is independent of γ and h , which may, therefore, also have negative imaginary values when it is not necessary to satisfy the boundary conditions on both parallel surfaces by choosing $\sin \gamma n$ and $\sin hn$ equal to zero, n being the distance separating top and bottom. Similarly the stresses over any one of the two other parallel boundary surfaces are the same at both ends only if $\sin \alpha l = \sin \beta m = 0$, so that the frequencies are determined although the boundary conditions are not completely satisfied.

The equation for the frequency has three roots, which are all real when σ is smaller than 0.26; for larger values of σ only one root is real.

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STUDIES ON REACTIONS RELATING TO CARBOHYDRATES AND POLYSACCHARIDES

XLVIII. ETHYLENE OXIDE AND RELATED COMPOUNDS: SYNTHESIS OF THE POLYETHYLENE GLYCOLS¹

BY STANLEY Z. PERRY² AND HAROLD HIBBERT³

Abstract

Four new methods are outlined for the synthesis of polyethylene glycols.

Ethylene glycol heated to 190° C. with 0.3% of its weight of iodine as a catalyst loses water to form diethylene- and other polyethylene glycols. The reaction is progressive and reversible. The yield of polyethylene glycols is about 25%.

The other three methods consist of modifications of a general method in which one mole of the dichloro derivative of a polyethylene glycol (the chlorine atoms forming the terminal groups) reacts with two moles of the monosodium salt of a polyethylene glycol. For this reaction the monosodium salt is obtained by one of the following methods: (a) direct solution of metallic sodium in the glycol; (b) reaction of metallic sodium with a methanol solution of the glycol in presence of anhydrous ether; (c) evaporation of a solution of the glycol and concentrated sodium hydroxide under diminished pressure.

Proof of the structure of these compounds is afforded by their analyses, their refractive indices, and their conversion into the corresponding dichloride by the action of thionyl chloride in pyridine solution.

Introduction

In the study of polymerized substances, two questions are of paramount importance: the mechanism by which the individual units polymerize and the nature of the forces joining the units in the final aggregate. These forces are now generally considered to be identical with normal valency forces, the resulting polymerized product representing in the vast majority of cases a successive combination or condensation of the building unit to form a long chain. Formerly the alternative views of ring formation by normal valency-, or of "molecular association" by residual valency, forces were fairly widely held, but have now been generally abandoned.

With a view to studying these forces and employing a substance of the simplest possible structure, an investigation was begun some eight years ago by the senior author on the mechanism of the polymerization of ethylene oxide. On the basis of the experimental data obtained by Staudinger (5,

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² Graduate student at McGill University and holder of a bursary (1929-1930) and a studentship (1931-1932) under the National Research Council of Canada.

³ Professor of Industrial and Cellulose Chemistry, McGill University.

p. 287) on the conversion of the ethylene oxide polymers into their acetates, he came to the conclusion that the "polyethylene oxides" are in reality polyethylene glycols. Assuming this to be true, then a stepwise synthesis of these glycols, permitting the preparation of the individual members of the polyethylene glycol series of very high molecular weight and in a pure state, would yield valuable products that would serve as reference substances with which to compare the individual fractions of the ethylene oxide polymers. A determination of their physical properties such as viscosity, freezing and boiling points should also provide data by means of which the validity of recent theories concerning the relation of these properties to the molecular size and state of aggregation could be checked.

The present paper describes the syntheses of the long-chain polyethylene glycols, while the nature and mechanism of the polymerization of ethylene oxide is reserved for a later communication.

Polyethylene glycols were first prepared by Lourenco in 1859 (3) by heating a mixture of ethylene glycol and ethylene bromide in a sealed tube at 115–120° C. He claimed to have isolated polyethylene glycols of a molecular weight as high as that of hexaethylene glycol (4). His experiment was repeated but no satisfactory results could be obtained.

Wurtz (6, 7) prepared polyethylene glycols by heating ethylene oxide with ethylene glycol or with water for several weeks.

Hibbert and Bilger (2) prepared polyethylene glycols, in fair yield, using the method previously employed by the former (1) in preparing polyglycerols. Ethylene glycol was heated in the presence of iodine, which acts as a condensation catalyst.

The known methods for the synthesis of polyethylene glycols proving unsuitable, it was necessary to develop a new method of synthesis in order to obtain pure products in good yield.

The general procedure adopted consisted in the primary formation of the monosodium salt of the glycol, followed by condensation of two moles of this salt with one mole of the dichloro derivative of a glycol, with elimination of two moles of sodium chloride and the formation of a new polyethylene glycol.

Preparation of the Sodium Salt of the Polyethylene Glycol

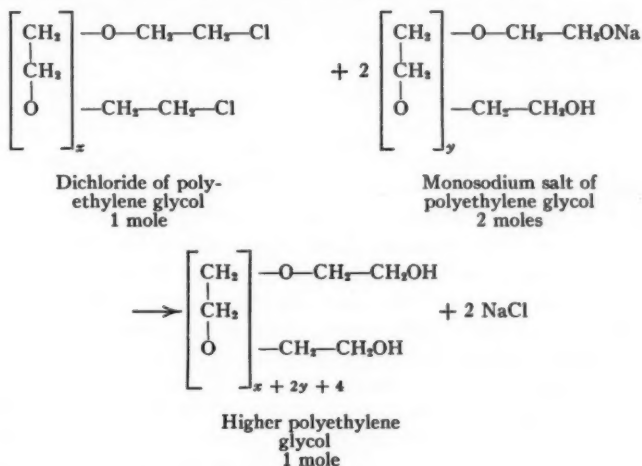
Attempts to prepare the monosodium salts by mixing the glycol with sodium hydroxide and removing the water by distillation under reduced pressure did not give satisfactory results.

The two most suitable methods for forming the monosodium salt consisted in the use of sodium methylate and metallic sodium respectively. In the former method one gram-atom of metallic sodium was dissolved in three times the excess of absolute methyl alcohol, and four to five gram-moles of the glycol added to the sodium methylate solution. The large excess of the glycol prevents the formation of the disodium salt. The partition of the

sodium which takes place between the glycol and the methyl alcohol can be forced over to the glycol side completely by distilling off the methyl alcohol. In the second method, metallic sodium is added to excess glycol at elevated temperatures.

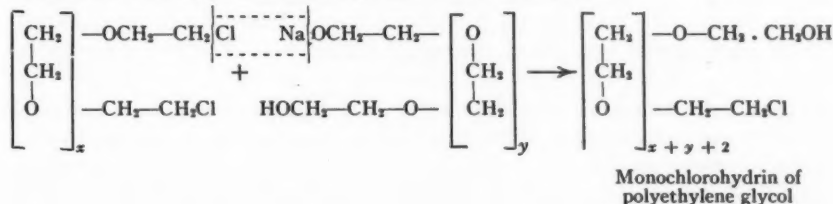
Primarily, the dichloride derivative of the glycols used in the synthesis was $\beta\beta'$ -dichloroethyl ether. However a method was later developed, using thionyl chloride in pyridine solution, whereby each polyethylene glycol could in turn be converted into the corresponding dichloride in good yield.

The general synthesis may be illustrated by the following:



where $x = 1, 2, 3, 4$, etc.; $y = 1, 2, 3, 4$, etc. Thus, for example, starting with $\beta\beta'$ -dichloroethyl ether and the monosodium salt of diethylene glycol, one obtains hexaethylene glycol.

The purification involves extraction of the crude condensation product with anhydrous ether in a continuous liquid extractor. The salt and any tarry matter are left undissolved. The ether extract is decolorized with charcoal, the ether removed and the residual liquid distilled at very low pressure, using a Langmuir mercury pump in series with a rotary oil pump. Several by-products were obtained depending on the conditions of the condensation. The monochlorohydrin was obtained when equimolecular proportions of monosodium salt and $\beta\beta'$ -dichloroethyl ether were used, thus:



If the temperature of condensation was maintained at about 200° C., vinyl compounds were formed by the action of the hot alkaline solution of the sodium derivative upon the $\beta\beta'$ -dichloroethyl ether.

The polyethylene glycols are very hygroscopic and must be protected from moisture at all times.

Indication of the structure of the long-chain polyethylene glycols is shown by the method of synthesis, and also by the fact that the two terminal hydroxyl groups may be replaced by chlorine. Analysis of the polyethylene glycols for carbon and hydrogen, as well as molecular weight determinations, yielded data in complete agreement with those obtained by analysis of the dichlorides. Refractive index measurements and boiling points of the synthetic polyethylene glycols and of their dichlorides were found to be in agreement with their respective positions in the long-chain polyethylene glycol series.

Experimental

Synthesis of Polyethylene Glycols—Iodine Method

A mixture of freshly distilled diethylene glycol (520 gm.) and iodine (1.5 gm.) contained in a three-necked flask fitted with a Hempel column, and connected in turn to a condenser, was heated to 190° C. for four hours. The contents was then subjected to fractional distillation, yielding 149 gm. of liquid boiling above 140° C./7.5 mm. Repeated fractionation yielded the following (total yield about 25%): (1) Triethylene glycol, 115.5–117° C./0.10 mm. (2) Tetraethylene glycol, 144.0–145.5° C./0.10 mm. (3) Pentaethylene glycol, 174.0–176.0° C./0.14 mm. (4) Residue, above 176.0°C./0.14 mm.

Triethylene glycol.—Found: C, 48.3; H, 9.5%; mol. wt. in ethylene dibromide, 156.0. Calcd.: C, 48.0; H, 9.3%; mol. wt. 150.1.

Tetraethylene glycol.—Found: C, 49.0; H, 9.3%; mol. wt. in ethylene dibromide, 206.0. Calcd.: C, 49.4; H, 9.3%; mol. wt. 194.1.

Pentaethylene glycol.—Found: C, 49.0; H, 9.1%; mol. wt. in ethylene dibromide, 238.0; n_D^{20} , 1.4617. Calcd.: C, 50.0; H, 9.2%; mol. wt. 238.2.

Synthesis of Tetraethylene Glycol—Sodium Method

Freshly distilled ethylene glycol (3,300 gm.) was introduced into a 5-litre three-necked flask, fitted with a mercury-seal mechanical stirrer, reflux condenser and thermometer. The system was protected from moisture by means of a calcium chloride tube. An atmosphere of dry nitrogen was maintained in the flask during the experiment. Freshly cut sodium (414 gm.—equivalent to 18 gram-atoms) was added through the condenser at a rate sufficient to maintain a brisk reaction at a temperature of 75° C. Eleven days was required to complete the reaction.

$\beta\beta'$ -Dichloroethyl ether (1287 gm.) was then added gradually from a dropping funnel to the above-mentioned reaction product at 65° C. during a period of three hours. Sodium chloride precipitated and a slight excess of

$\beta\beta'$ -dichloroethyl ether (36 gm.) was added towards the end to ensure complete reaction with the sodium salt. The dark brown product was decolorized by shaking its alcoholic solution repeatedly with Darco charcoal. Fractional distillation yielded 740 gm. of tetraethylene glycol, b.p. $160^{\circ}\text{C}/2-3\text{ mm.}$ Yield, 39%. Found: C, 49.0; H, 9.3%; mol. wt. in ethylene dibromide, 206.0; $n_D^{20^{\circ}\text{C.}}$, 1.4593. Calcd.: C, 49.4; H, 9.3%; mol. wt., 194.1.

Synthesis of Hexaethylene Glycol—Sodium Methylate Method

Diethylene glycol (1500 gm.), acetone-free methyl alcohol (125 gm.) and absolute ether (200 cc.) were introduced into a two-litre three-necked flask fitted with mechanical stirrer and reflux condenser and maintained at a temperature of 40°C. Freshly cut sodium (93 gm.) was added gradually, during the course of seven hours, through the condenser. On cooling to room temperature, colorless crystals of the sodium salt separated from solution and were removed by filtration. The solid and the adhering liquid (amounting to 300 gm. and containing 8.8% of hydrolyzable alkali) were then condensed with the theoretical quantity of $\beta\beta'$ -dichloroethyl ether in the proportion of two moles of the sodium salt to one mole of the ether. The condensation was carried out in the same manner as in the sodium method, the temperature being maintained at 70°C. until tests indicated that the reaction mixture was neutral. The product was extracted with dry ether in a continuous liquid extractor in order to free it from sodium chloride formed in the reaction. After decolorizing with Darco charcoal, the liquid was fractionally distilled under diminished pressure and yielded 76.9 gm. of hexaethylene glycol. B.p. $158-160/0.009\text{ mm.}; 166-168/0.015\text{ mm.}$ Yield, 49.75%. Found: C, 51.2; H, 9.3%; mol. wt. in ethylene dibromide, 297; $n_D^{20^{\circ}\text{C.}}$, 1.4637. Calcd.: C, 51.0; H, 9.2%; mol. wt. 282.

Synthesis of Hexaethylene Glycol—Sodium Hydroxide Method

Diethylene glycol (600 gm.) was introduced into a one-litre three-necked flask, fitted with dropping funnel and a mechanical stirrer capable of operating under diminished pressure, the flask being connected through a drying tower to a water pump. The system was evacuated and sodium hydroxide (120 gm.), dissolved in the smallest quantity of water, was added gradually with stirring. The reaction mixture warmed spontaneously and some effervescence was observed. When the reaction had subsided, the contents was heated to 100°C. for six hours, after which time no further evolution of water vapor could be detected. The reaction product was cooled and the theoretical quantity of $\beta\beta'$ -dichloroethyl ether (216 gm.) was then added, and the temperature raised to 72°C. until the solution was neutral. The crude product was purified as in the sodium methylate method. Yield, 240 gm.

Synthesis of the Dichloride of Tetraethylene Glycol

Tetraethylene glycol (30 gm.), b.p. $144.0-145.5/0.10\text{ mm.}$, dissolved in pyridine (25 gm.) was introduced into a three-necked flask fitted with a mechanical stirrer, reflux condenser and dropping funnel. Thionyl chloride

(38 gm.) was then added at room temperature through a dropping funnel during a period of one and one-half hours. Several pieces of porous tile were added and the reaction product heated to 60° C. as long as sulphur dioxide was evolved. The dark brown product was poured into three times its own volume of cold water and extracted several times with ether. The ether layer was neutralized with sodium bicarbonate, dried over sodium sulphate, filtered and the ether evaporated. Distillation of the residual product yielded 27.5 gm. of the dichloride, b.p. 107.5–108.5° C./1 mm. Yield, 77%. Found: Cl (Stepanov volumetric method), 30.4, 30.5%. Calcd.: 30.7%.

Synthesis of the Dichloride of Hexaethylene Glycol

Hexaethylene glycol dichloride was prepared in the same manner using hexaethylene glycol (33.0 gm.), pyridine (18.5 gm.) and thionyl chloride (27.8 gm.). B.p. 146.5–148° C./1 mm.; yield, 28.7 gm. or 77.6%. Found: Cl, 22.3, 22.2%. Calcd.: Cl, 22.2%.

Synthesis of Octaethylene Glycol

To a mixture of redistilled diethylene glycol (200 gm.) and dry ether (50 cc.), contained in a three-necked flask, fitted with mechanical stirrer and reflux condenser, was added metallic sodium (4.78 gm.) in small pieces, during the course of two hours. Stirring was maintained throughout and no heat was applied (sufficient being generated in the reaction). Tetraethylene glycol dichloride (23 gm.) was then added from a dropping funnel during a period of one hour, the temperature being maintained at 90–100° C. during the addition, and then raised to 160° C. for two hours, when a neutral reaction was indicated. The product was extracted with ether and decolorized as in previous experiments. On fractional distillation under diminished pressure, octaethylene glycol, b.p. 206–209° C./0.015–0.018 mm., was obtained. Yield, 21.8 gm., or 59%.

Synthesis of Octaethylene Glycol Dichloride

Octaethylene glycol (10.8 gm.) was dissolved in pyridine (4.6 gm.) and the mixture treated with thionyl chloride (6.9 gm.) (1 : 2 : 2 moles) in the manner employed previously. The dichloride was obtained in the form of a colorless, virtually odorless oil, b.p. 199.5–202° C./3–4 mm. Yield, 6.1 gm. Found: Cl, 17.2, 17.3%. Calcd. for $C_{16}H_{32}O_7Cl_2$: Cl, 17.4%.

Synthesis of Decaethylene Glycol

A mixture of diethylene glycol (171 gm.) and ether (100 cc.) was treated with 3.5 gm. of sodium (1/11 mole), in the manner described above, until the sodium had dissolved. Hexaethylene glycol dichloride (24.8 gm.) was then added, and the temperature maintained first at 70° C. for five hours, then at 100° C. for four hours and finally at 160° C. for forty hours. The neutral reaction product treated in the usual manner yielded a colorless oil, b.p. 220–223° C./0.010 mm. Yield, 68.5%.

Synthesis of Decaethylene Glycol Dichloride

In the same manner, decaethylene glycol (10 gm.) was dissolved in pyridine (3.5 gm.) and treated with thionyl chloride (5.2 gm.). The reaction product was light in color, but on heating to 50° C. it darkened quite rapidly. Fractional distillation yielded 3.1 gm. of the dichloride, b.p. 205–208° C./0.015 mm. Yield, 28.7%. Found: Cl, 14.6, 14.6%. Calcd. for $C_{20}H_{40}O_9Cl_2$: Cl, 14.3%.

Acknowledgment

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THE DECOMPOSITION OF NITROUS OXIDE ON THE SURFACE OF PLATINUM

II. THE EFFECT OF FOREIGN GASES¹

By E. W. R. STEACIE² AND J. W. MCCUBBIN³

Abstract

Further experiments have been made on the kinetics of the decomposition of nitrous oxide on the surface of platinum. Observations on the effect of foreign gases confirm the previous conclusion that inert gases may exert a surprisingly large retarding effect by hindering the diffusion of the reactant to the more remote parts of a porous catalyst.

Adsorption measurements have also been made, and their bearing on the mechanism of the reaction is discussed.

Introduction

In a previous paper (1) an investigation of the retarding action of oxygen on the decomposition of nitrous oxide on platinum was described. It was shown that with oxygen-nitrous oxide mixtures the order of admission of the gases to the reaction vessel had a marked effect on the rate of reaction. Various other rather complicated effects were observed, and it was concluded that, in addition to its normal retardation of the reaction by adsorption, oxygen also retards the reaction by hindering the diffusion of the reactant to the more remote parts of a porous catalyst. If this explanation is correct, there are two courses of investigation which should prove illuminating. The first is the effect of the addition of inert gases on the rate of reaction, with and without the addition of oxygen. The second is the use of a platinum catalyst with a less porous structure than sponge platinum.

Furthermore, the previous investigation proved that oxygen formed in the reaction has a much more pronounced effect on the rate than has added oxygen. This is difficult to explain, and it was thought that adsorption measurements might throw some light on the process.

Experimental

Rates of reaction were investigated with the apparatus previously described, and adsorption measurements were made with an apparatus previously used by Steacie and Stovel (2). For the method of calculating and reporting the results, etc., reference should be made to the previous paper.

The Effect of Added Nitrogen

Results

The results with added nitrogen are summarized in Table I.

These results confirm completely the conclusions drawn from previous experiments with oxygen, *viz.*, that the foreign gas may under proper conditions exert a strong retarding effect by hindering diffusion to the more remote parts

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TABLE I

THE EFFECT OF ADDED NITROGEN

Catalyst No. 3. Temperature, 570° C. $b = 0.635$. Initial partial pressure of $N_2O = 6.00$ cm.

Nitrogen added first, cm.	Oxygen added first, cm.	Nitrogen added with the N_2O , cm.	K	Nitrogen added first, cm.	Oxygen added first, cm.	Nitrogen added with the N_2O , cm.	K
—	—	—	1.395	—	39.90	15.02	0.087
—	—	20.00	1.240	16.95	22.90	—	0.025
39.85	—	—	0.508	22.10	17.95	—	0.029
39.90	—	—	0.362	27.60	12.35	—	0.035
—	39.70	—	0.015	32.10	7.85	—	0.046
—	39.90	5.65	0.079	34.05	5.95	—	0.069
—	39.90	12.77	0.078	35.95	3.90	—	0.057

of a porous catalyst. Thus when nitrogen is added mixed with nitrous oxide there is a very slight decrease in the velocity constant. If, however, nitrogen is added first, and thus the pores of the catalyst are filled with it, there is a three- or four-fold diminution in K . On the other hand, if oxygen is admitted to the catalyst initially, the addition of nitrogen to the nitrous oxide added later will increase the rate, owing to the increased compression of the gas into the pores of the catalyst.

Experiments with a Platinum Gauze Catalyst

One obvious way to check the foregoing conclusions is to use a catalyst which has a non-porous structure. Experiments were therefore made with a catalyst consisting of 12 sq. in. of 60 mesh platinum gauze, contained in a silica reaction vessel of approximately 70 cc. capacity.

At 570° C. the rate was now too small, on account of the decreased surface, to make it practicable to carry the runs to completion, and the relative rates were therefore inferred by comparing the amounts reacting in a definite time. The data are summarized in Table II. It will be seen that, in agreement with the previous conclusions, nitrogen

TABLE II

PLATINUM GAUZE CATALYST

570° C. Initial partial pressure of $N_2O = 6.00$ cm.

Added gases	% of nitrous oxide decomposed in 4 min.
None	19.10
5.55 cm. of oxygen before the N_2O	4.60
3.50 cm. of oxygen before the N_2O	6.23
1.45 cm. of oxygen before the N_2O	11.21
0.95 cm. of oxygen before the N_2O	14.70
0.40 cm. of oxygen before the N_2O	18.58
8.85 cm. of oxygen added with the N_2O	3.15
5.40 cm. of oxygen added with the N_2O	6.06
4.20 cm. of oxygen added with the N_2O	9.60
2.13 cm. of oxygen added with the N_2O	9.16
1.25 cm. of oxygen added with the N_2O	11.46
20.15 cm. of nitrogen before the N_2O	16.32
19.80 cm. of nitrogen added with the N_2O	20.50

now has virtually no effect on the rate. With oxygen it now makes no appreciable difference whether it is added before or with the nitrous oxide.

Other Foreign Gases

The results of experiments with added helium and carbon dioxide with the porous catalyst are given in Fig. 1. These gases have only a small effect on

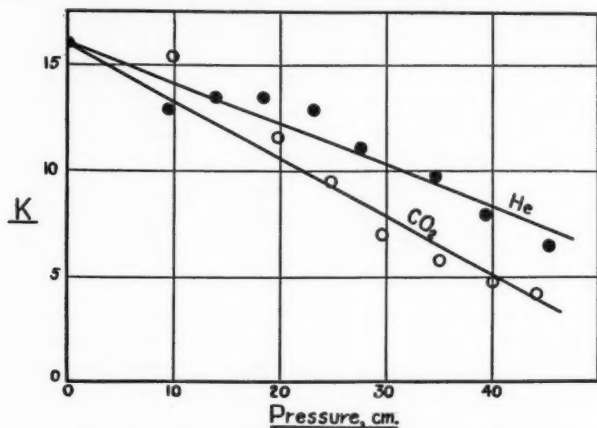


FIG. 1. The effect of foreign gases on the rate of reaction.

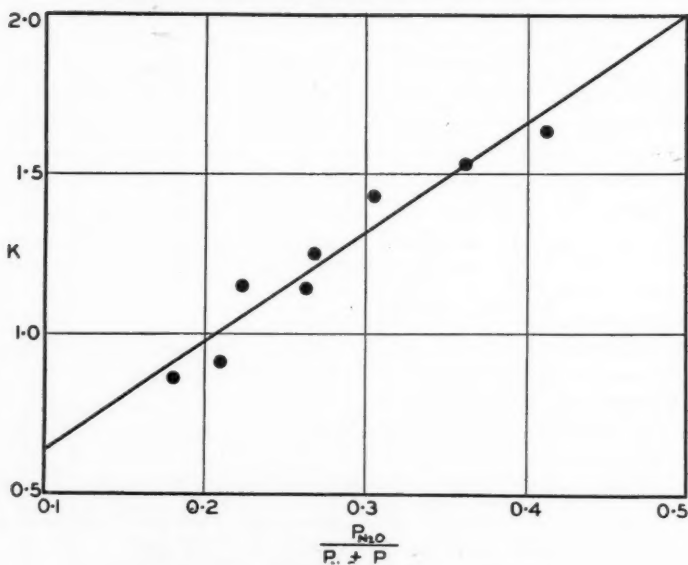


FIG. 2. The retardation of the reaction by helium.

the rate. If their effects are due solely to diffusion processes, then

$$K \propto \frac{P_{N_2O}}{P_{N_2O} + P_{\text{foreign gas}}} \cdot *$$

*This expression may be derived in a manner analogous to that used in dealing with the effect of foreign gases on chain reactions. See, for example, Melville, H. W., *Trans. Faraday Soc.* 28: 814-818. 1932.

If K is plotted against the right-hand side of the above expression, good straight lines are obtained for both helium and carbon dioxide. The results for helium are shown in Fig. 2. Furthermore, the ratio of the slopes of the lines for the two gases should theoretically be 0.63 (with some uncertainty since molecular diameters are involved). The experimental value of the ratio is 0.6.

The Effect of Water Vapor

A number of experiments were made in the presence of small amounts of water vapor (up to 4 cm. partial pressure). When the water vapor was added with nitrous oxide or with nitrous oxide-oxygen mixtures there was no appreciable effect upon the velocity constant. When the water vapor was admitted prior to the admission of the nitrous oxide, however, there appeared to be a small increase in rate up to 1 cm. of water vapor, followed by a decrease as the amount of water was increased. The effect, however, was not very much greater than the experimental error (although it was always observed, and is probably real). In consequence it does not appear to be worth while giving the results in detail.

Adsorption Measurements

A series of adsorption measurements was made with the sponge catalyst at the temperatures used in the investigation of the decomposition. The experimental procedure was the same as that used previously, nitrogen being used to calibrate the system. A typical isotherm for oxygen at 570° C. is shown in Fig. 3, Curve 1. The adsorption occurred instantaneously. Heating to redness during evacuation, or burning off with hydrogen did not alter the adsorption in the following run, and hence the adsorption is reversible to within the experimental error at this temperature.

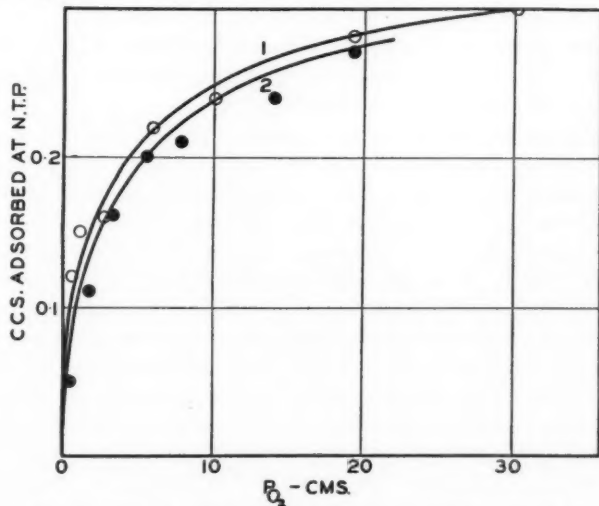


FIG. 3. The adsorption of oxygen by a porous platinum catalyst.

The adsorption of oxygen formed by the decomposition of nitrous oxide was also investigated by adding a measured amount of nitrous oxide to the catalyst and noting the difference between the observed and calculated pressures after the reaction had reached completion. This was done at various initial nitrous oxide pressures, and thus the isotherm shown in Fig. 3, Curve 2, was obtained. The presence of nitrogen was assumed to be without effect on the adsorption of oxygen. It will be seen that the two curves in Fig. 3 are identical within the experimental error. This is rather surprising in view of the different retarding effects of the two "types" of oxygen in the experiments on the rate of reaction. It must be concluded that the oxygen formed during the reaction is not irreversibly adsorbed to any great extent.

The adsorption of carbon dioxide was not detectable at 570° C.

At 250° C., which is well below the temperature of decomposition, there was no measurable adsorption of nitrous oxide on the catalyst. From this result, as well as from the similarity of nitrous oxide and carbon dioxide, we may conclude that the adsorption of nitrous oxide on platinum at 570° C. is extremely small. Hence the previous assumptions regarding the mechanism of the decomposition, *viz.*, small adsorption of nitrous oxide and large adsorption of oxygen, are fully verified.

Discussion

The main facts established in this and in the previous investigation which require explanation are those connected with the retardation of the reaction by oxygen. These facts are:

- (1). Oxygen formed in the reaction retards it, the rate being given by

$$-\frac{d(\text{N}_2\text{O})}{dt} = \frac{K(\text{N}_2\text{O})}{1 + b(\text{O}_2)}.$$

- (2). Oxygen added to the reaction mixture diminishes K , and thus retards the reaction. (O_2) in the denominator, however, refers only to oxygen formed in the reaction, and not to oxygen added initially.

- (3). Adsorption measurements show no appreciable difference between the adsorption of oxygen formed in the reaction and that of oxygen added initially. It may therefore be concluded that at least the major part of the oxygen formed in the reaction is not irreversibly adsorbed.

- (4). The reversibility of the adsorption process is further confirmed by the fact that the amount of oxygen adsorbed is not altered by evacuation at a red heat or by burning off with hydrogen. It is also confirmed by the fact that in reaction rate runs if the evacuation between runs is very short (one or two minutes) the rate of the following run is not altered.

If we assume that the surface is not uniformly active, and that the reaction is retarded by molecular oxygen on the less active parts and by atomic oxygen formed in the reaction on the more active parts, we could explain different degrees of retardation by the two "types" of oxygen. Such an explanation, however, is at variance with (a) the reversibility of the adsorption process,

since the oxygen formed in the reaction could have distinctive properties only provided that it never left the surface, and (b) with the fact that the form of the reaction velocity curve (as shown by the rate equation) is not altered *at all* by the addition of oxygen, although the rate may be cut down to a few per cent of its former value.

Objection (b) could be overcome if we assumed that both kinds of oxygen are adsorbed on the *active* part of the surface, but that atomic oxygen formed in the reaction is irreversibly adsorbed and is not displaced by nitrous oxide, while added oxygen is molecularly adsorbed, and is displaced, but with difficulty, by nitrous oxide. This, however, does not meet objection (a).

No matter what explanation of this kind is proposed, two facts seem quite irreconcilable, *viz.*, (a) oxygen can retard the reaction in two different ways, (b) the adsorption process is rapidly reversible.

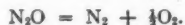
Now it should be noticed that the rate equation

$$-\frac{d}{dt}(\text{N}_2\text{O}) = \frac{K(\text{N}_2\text{O})}{1 + b(\text{O}_2)},$$

where (O₂) refers only to oxygen formed in the reaction, is really of the form

$$-\frac{d}{dt}(\text{N}_2\text{O}) = \frac{K(\text{N}_2\text{O})}{1 + f(\text{amount of N}_2\text{O decomposed})}.$$

It is therefore possible that the retardation of the reaction by oxygen formed in it is partly real (inasmuch as added oxygen retards it also), but is mainly fictitious and due merely to the fact that $f(\text{amount of N}_2\text{O decomposed})$ is identical with $f(\text{amount of oxygen formed})$. Hence the retardation of the reaction by any other substance produced in it would be indistinguishable from retardation by oxygen. Now the over-all reaction is



Nitrogen has already been shown to be virtually without effect on the rate. It is, however, possible that a trace of some other nitrogen oxide, formed in a side reaction, may poison the surface. Or, the surface might be poisoned by a trace of the oxidation product of some impurity introduced with the nitrous oxide. In any case, whatever the explanation may be, the present results make it appear doubtful that oxygen formed in the reaction really retards it in the manner which the usual rate equation indicates.

Acknowledgment

We wish to express our indebtedness to the National Research Council of Canada for a bursary awarded to one of us (J. W. McC.) during the tenure of which this work was performed.

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THE POLARIZATION OF LIQUIDS AND THEIR SATURATED VAPORS IN THE CRITICAL TEMPERATURE REGION¹

By J. MARSDEN² AND O. MAASS³

Abstract

The values of the so-called polarization of methyl ether (liquid and saturated vapor) and propylene (liquid and saturated vapor), from room temperature to the critical temperature, are given. In both liquids this polarization is independent of the temperature to within a few degrees of the critical temperature. Calculations show that the polarizations of a liquid and its saturated vapor may be equal above the critical temperature, even though the dielectric constants of the liquid and its saturated vapor, as well as their densities, are different.

Introduction

In an earlier paper (4) a technique was described for the measurement of the dielectric constants of liquids and their saturated vapors, and the dielectric constants of methyl ether and propylene were given. These values are used to calculate the variation of the molar polarization with temperature.

In recent years the work of Smyth and co-workers has shown the importance of dielectric constant studies in the field of molecular structure. Apart from this, interesting information might be obtained regarding the nature of the liquid and gaseous states of aggregation. In this connection, studies in the region of the critical temperature are obviously pertinent. Smyth (6) has pointed out the importance of a study of this kind. It is probable that the difficulty in experimental technique is the reason why so little work has been done on dielectric constant measurements of liquid and saturated vapor in the region of the critical temperature. Not only is the high pressure developed at the critical temperature a difficulty, but also the variation of dielectric constants with temperature is very marked. Furthermore, for the interpretation of the results, the densities of the liquid and the saturated vapor must be known.

Eversheim (2, 3) measured the dielectric constant of hydrogen sulphide, liquid and saturated vapor, over a temperature range that extended beyond the critical temperature. The interpretation of his results, so far as the discontinuity at the critical temperature is concerned, has been discussed (4). Although his dielectric constant determinations are sufficiently accurate for the calculation of polarization, lack of data regarding the density makes it impossible to use his values for this purpose. Verain (9) carried out a similar investigation on the dielectric constant of carbon dioxide. In this case, the values are not sufficiently accurate, in the region of the critical temperature, to be of any material use for polarization calculations.

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In view of the investigations that have been carried out in this laboratory regarding what might be called the persistence of the liquid state above the critical temperature, the examination of the polarization at and beyond the critical temperature of the medium above and below the disappearing meniscus is of particular interest.

Results and Discussion

For purposes of the discussion of results, the following relations and their significance are reproduced from papers of Smyth (6, 7). If the molecules of a substance are free to assume a random orientation, as in the gaseous state at low pressures, the molar polarization is given by the following equation:

$$P = \frac{\epsilon - 1}{\epsilon + 2} \times \frac{M}{D} = \frac{4\pi}{3} \nu N + \frac{4\pi N}{3} \frac{\mu^2}{kT}$$

where ϵ = dielectric constant, M = molecular weight, N = Avogadro's number, ν = molecular polarizability, k = molecular gas constant, T = absolute temperature, and μ is the electric moment. The expression $\frac{4\pi}{3} N\nu$ is the polarization due to the displacement of electrons and atoms or groups of atoms in the molecule. If the influence of atoms or groups of atoms can be neglected, denote the expression $\frac{4\pi}{3} \nu N$ by P_E , which is the polarization due to the displacement of electrons. P_E can be calculated from the molar refraction of light at infinite wave-length.

The expression $\frac{4\pi}{3} \frac{\mu^2}{kT}$ is the polarization due to the permanent moment of the molecule, orientated by an applied electric field, and may be called P_M . In the derivation of the expression for P_M , it has been assumed that the freedom of molecules to orientate, in an applied electric field, is unhampered by the orientating influence of the molecules upon one another in the absence of an electric field. The ability of the molecules to orientate will be opposed by increasing their kinetic energy.

Tables I and II show the values of the polarization of methyl ether, liquid and saturated vapor, together with the densities and dielectric constants necessary for the calculation of the polarization. The densities of methyl ether were taken from the data of Cardoso

TABLE I
THE RELATION BETWEEN POLARIZATION OF METHYL
ETHER LIQUID AND TEMPERATURE

Temp., °C.	$\frac{1}{T}$	Dielectric constant	Density	P
24.5	.003362	5.034	0.6548	40.34
37.3	.003222	4.732	0.6336	40.30
50.5	.003091	4.424	0.6104	40.22
60.6	.002997	4.179	0.5924	40.00
69.95	.002915	3.949	0.5744	39.74
80.30	.002830	3.712	0.5512	39.66
90.20	.002755	3.474	0.5240	39.73
100.30	.002679	3.227	0.4920	39.88
104.9	.002647	3.114	0.4758	40.02
109.0	.002618	2.993	0.4608	39.90
116.9	.002565	2.749	0.4260	39.81
120.6	.002541	2.615	0.4032	39.96
123.2	.002524	2.492	0.3792	40.36
125.0	.002513	2.369	0.3518	41.02
126.1	.002506	2.257	0.3260	41.72

TABLE II
THE RELATION BETWEEN THE POLARIZATION OF METHYL
ETHER GAS AND TEMPERATURE

Temp., °C.	$\frac{1}{T}$	Dielectric constant	Density	P
59.2	.003010	1.225	0.0312	103.0
80.0	.002833	1.262	0.0490	75.5
100.0	.002681	1.343	0.0824	57.35
104.1	.002652	1.364	0.0918	54.30
106.1	.002638	1.377	0.0960	53.55
109.4	.002615	1.404	0.1044	52.36
114.5	.002581	1.462	0.1202	51.12
119.5	.002548	1.538	0.1424	49.18
122.0	.002532	1.590	0.1592	47.54
123.0	.002525	1.605	0.1680	46.01
124.8	.002514	1.667	0.1894	44.23
126.0	.002506	1.760	0.2139	43.52

TABLE III
THE RELATION BETWEEN THE POLARIZATION OF PROPY-
LENE LIQUID AND TEMPERATURE

Temp., °C.	$\frac{1}{T}$	Dielectric constant	Density	P
21.0	.003401	1.873	0.5150	18.40
25.1	.003356	1.864	0.5071	18.53
29.9	.003301	1.852	0.4982	18.66
34.5	.003252	1.843	0.4895	18.84
39.2	.003203	1.824	0.4804	18.85
45.0	.003145	1.795	0.4682	18.81
50.2	.003094	1.779	0.4570	18.96
54.8	.003051	1.742	0.4462	18.70
65.0	.002959	1.690	0.4201	18.72
67.9	.002933	1.669	0.4115	18.63
71.4	.002904	1.654	0.4004	18.79
75.7	.002867	1.625	0.3850	18.83
81.1	.002825	1.579	0.3620	18.79
83.5	.002805	1.547	0.3500	18.52
87.6	.002773	1.493	0.3218	18.46
89.9	.002756	1.445	0.2950	18.41
90.7	.002750	1.419	0.2772	18.58
91.4	.002744	1.375	0.2530	18.47
91.6	.002742	1.350	0.2390	18.38

TABLE IV
THE RELATION BETWEEN THE POLARIZATION OF PROPY-
LENE GAS AND TEMPERATURE

Temp., °C.	$\frac{1}{T}$	Dielectric constant	Density	P
31.8	.003281	1.114	0.0300	51.30
50.8	.003088	1.134	0.0480	37.45
69.5	.002920	1.144	0.0770	25.01
72.4	.002895	1.151	0.0830	24.28
75.9	.002865	1.165	0.0915	23.95
80.0	.002832	1.182	0.1050	22.90
82.2	.002816	1.194	0.1140	22.40
84.4	.002797	1.203	0.1245	21.41
89.9	.002756	1.254	0.1715	19.14
90.2	.002754	1.258	0.1760	18.91
91.1	.002747	1.279	0.1930	18.53

and Coppola (1). Tables III and IV show the values of polarization of propylene, liquid and saturated vapor. Winkler's (10) and Pall's (5) density values for propylene were used.

The assumptions involved in the Debye equation are not valid either for pure liquids or for vapors whose pressure is constantly increasing with rise in temperature. The empirical results, in making polarization calculations, are however of interest. In the first place, for both liquids the polarization is independent of the temperature to within a few degrees of the critical temperature. This has been observed by Smyth and co-workers (8) for chlorobenzene and ethyl bromide as well as the non-polar hexane. It was in this connection that Smyth indicated that it would be interesting to extend the investigation through the critical temperature region. It would, of course, be of special interest to compare the polarization at infinite dilution through this temperature range; however, certain deductions can be made from the data involving the polarization of the saturated vapor.

In the case of liquid propylene, the so-called polarization remains constant up to the critical temperature, in a surprising manner, when it

is remembered that near the critical temperature both the density and the dielectric constant are undergoing enormous variations. The polarization values for the saturated vapor decrease in a linear manner until a temperature of 70° C. is reached. At this temperature, the density increase of the vapor begins to become very marked; as a result the density increases more rapidly than $(\epsilon - 1)$, with rise in temperature, thus bringing about the inflection in the curve.

The most important deduction indicated by Fig. 1 is that the polarizations of the liquid and the saturated vapor become identical at the critical temperature. At first sight, this might appear to be contrary to the observations

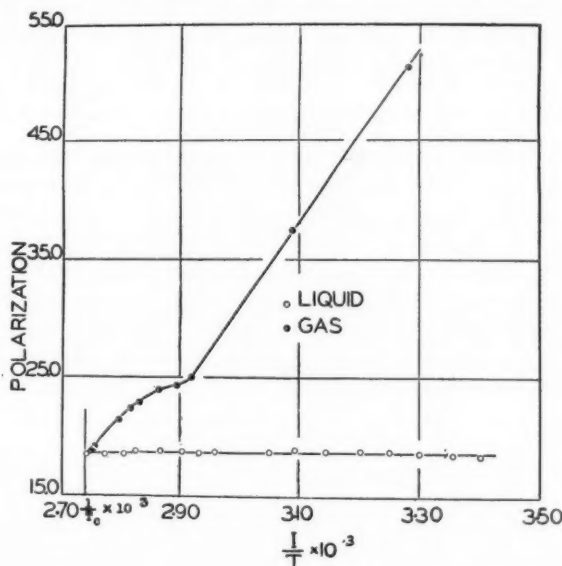


FIG. 1. The polarization-temperature relation for propylene liquid and gas.

made by the authors that the dielectric constants of the medium above and below the disappearing meniscus are of different magnitudes, for temperatures appreciably above the critical temperature. It must be remembered, however, that the densities of liquid and saturated vapor are also different, at and above the critical temperature, and that it is possible for these two factors to compensate each other in such a way that the polarizations of the medium above and below the point of disappearance of the meniscus might be identical.

Winkler and Maass (10) showed that the difference in density of liquid and gas above the critical temperature depended on the amount of material in the bomb. However, if it is assumed that the conditions of mass per volume under which the dielectric constants were measured are approximately the same as the conditions under which the densities were measured by Winkler,

calculations can be made of the polarizations of the medium above and below the point at which the meniscus disappeared. The dielectric constant values are taken from Table VI of a former paper by the authors (4).

The values of the polarization, shown in Table V, are identical within the accuracy under which the measurements, on which the calculations of polarization are based, were made.

TABLE V

POLARIZATION VALUES OF PROPYLENE, LIQUID AND SATURATED VAPOR, ABOVE THE CRITICAL TEMPERATURE

Temp., °C.	ϵ_{liquid}	ϵ_{gas}	D_{liquid}	D_{gas}	P_{liquid}	P_{gas}
91.9	1.331	1.279	0.2320	0.1990	18.0	18.0
93.1	1.318	1.292	0.2160	0.2050	18.6	18.2
96.4	1.314	1.310	0.2130	0.2093	18.7	18.8

To sum up, it has been shown that it is possible that the polarizations of liquid and saturated vapor can very well be identical at the critical temperature, although the density and the dielectric constant values show a discontinuity.

In Fig. 2 the polarization curve of the methyl ether saturated vapor is similar in form to that of propylene. The gradient is much steeper, so that the lowest temperature point had to be omitted. At lower temperatures the curve is linear, and the inflection again occurs where the density of the vapor shows a marked increase.

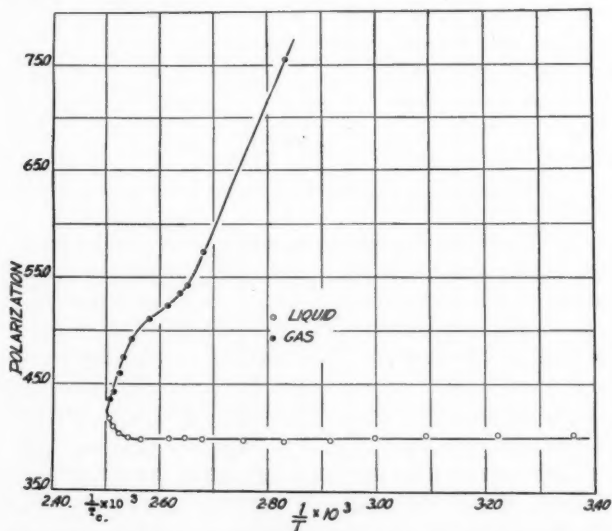


FIG. 2. The polarization-temperature relation for methyl ether liquid and gas.

The polarization of the liquid is again constant to a remarkable extent, but, in this case, at 4° C. below the critical temperature the polarization of the liquid increases to meet that of the saturated vapor at the critical temperature.

It is a matter of considerable interest that the polarization, or rather that the relation $\frac{\epsilon - 1}{\epsilon + 2} \times \frac{M}{D}$, when plotted against $\frac{1}{T}$, should remain constant over such a wide temperature range. It appears almost as though the decrease in polarization with rise in temperature, due to increased thermal agitation, was compensated for in the liquid by a decreased influence of the attraction of molecules upon one another. That the two effects exactly compensate each other cannot be fortuitous, and if the explanation is correct, it will be of considerable value to obtain further data of this nature, such as has been presented in this paper.

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THE LIQUID DENSITIES OF PROPYLENE AND METHYL ETHER AS DETERMINED BY A MODIFIED DILATOMETER METHOD¹

BY D. B. PALL² AND O. MAASS³

Abstract

A modification of the dilatometer method for measuring the density of liquids which can be applied over a large temperature range and up to the region of the critical temperature is described. The densities of methyl ether and propylene have been measured over the temperature range 7°–120° C. and 20°–88° C. respectively, with an accuracy of 1 part in 2000. A comparison is made with the data of other investigators. Application of the data to the law of corresponding states shows that the law holds to within the accuracy attained up to temperatures at least 0.96 of the critical.

Introduction

The work described was undertaken for a twofold purpose. First, accurate data on the densities of propylene and methyl ether were required in connection with a number of investigations carried out in this laboratory. Second, an experimental technique involving several novel features was to be tested.

It has been found that above the critical temperature the density of the medium below the place of meniscus disappearance is greater than that above. In investigating this the McBain-Bakr balance with attached float served admirably, as a relative change in density could be measured accurately in the region from just below to 15° above the critical temperature. However, a McBain-Bakr balance with attached float could not be used with accuracy for the measurement of liquid density from 70° below the critical temperature to the critical temperature. It happens that such measurements are of particular interest at the moment.

The new feature in the dilatometer method to be described involves the determination first of the volume of the medium, and then its weight, by evaporating and condensing the medium into a small glass bulb, which was then sealed off. This made possible a permanent set-up of a dilatometer in a thermostat, and furthermore, as will be seen in the detailed description of procedure, the dead space of vapor could be reduced to a minimum.

The two substances investigated were propylene and methyl ether. The liquid densities of these substances have been measured by Cardoso and Coppola (2), Maass and Wright (4), Maass, Boomer and Morrison (3), and Winkler and Maass (7). A comparison will be made here of the data obtained by the writers with those of the other investigators.

As the range of temperature covered is a large one, it was of interest to compare the densities in correlation with the requirements of the law of corresponding states.

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Experimental

Propylene was prepared by the catalytic dehydration of isopropyl alcohol by alumina at 350° C. Commercial methyl ether was used. Both were carefully purified by successive distillations in vacuum, as described by Maass and Wright (4), and Tapp, Steacie and Maass (6). The preparation apparatus was equipped with a manometer and a distillation bulb with a magnetic stirrer. After purification the material was condensed into a bulb with a stopcock. This bulb (A) was then detached and glass-sealed to the apparatus (Fig. 1) at C.

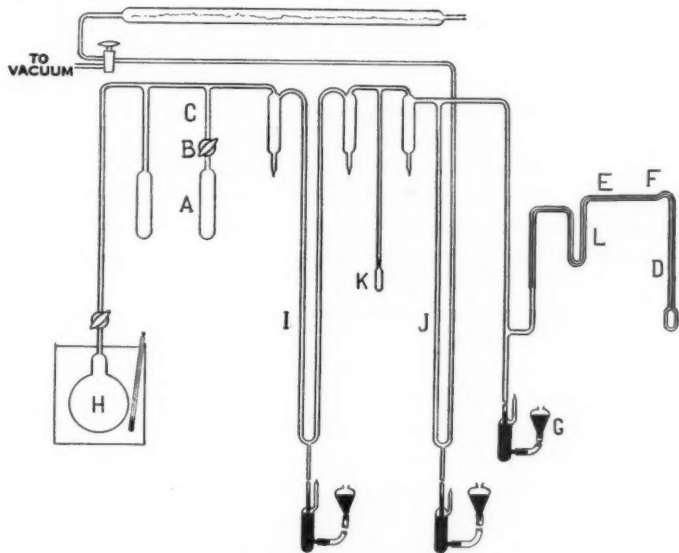


FIG. 1. Diagram of modified dilatometer apparatus.

The dilatometer *D* in which the volumes were measured was constructed of Pyrex capillary and bomb tubing, in such a manner as to withstand the high pressures obtaining near the critical temperature. The volume of the bulb was 2.5 cc. and the inside diameter of the capillary tubing was 1.7 mm. An error of 0.5 mm. in reading the height of the meniscus corresponds to an error of one part in 2000 in the volume calculated. Actually, by means of a telescope, readings were made to within 0.1 mm.

The dilatometer was calibrated by introducing weighed quantities of mercury, and measuring the heights on the scale attached to the capillary. Meniscus corrections were made. These are difficult to estimate accurately, but owing to the comparatively large volume* of the dilatometer give rise to a relatively unimportant correction.

* 2.5 cc. in this case as compared to 0.07–0.11 cc. in the investigation by Cardoso and Coppola.

The capacity of the bath was four gallons. Temperature could be controlled to $1/50^\circ$ by means of external rheostats. The standardized thermometers were calibrated to within $1/20^\circ$ below 100° , and to $1/10^\circ$ above this temperature.

The supporting arm, *E*, of the dilatometer was fastened through the side of the bath in such a manner that all the tubing to the right of *E* was immersed in the bath liquid. This horizontal part of the tubing was provided with a scale similar to that used for the dilatometer proper, and calibrated so that the volume corresponding to any point on the scale was known. A slight upward bend was made in the capillary at *F*. A 3 cm. length of tubing on either side of *F* was wound with a nichrome element, making it possible to heat this portion separately.

In making a run, an amount of material estimated to have a volume of 2.5 cc. at the lowest temperature at which it was desired to make readings was distilled into the dilatometer bulb. This amount could be approximately predetermined by filling the calibrated volume *H* with gas at the proper pressure and temperature. The stopcock *B* was then closed and the leveling bulb *G* raised until mercury had filled the U-tube *L* and passed up to the point *F*. The mercury in the U-tube was then frozen by placing around it a Dewar flask filled with a mixture of dry ice and acetone.

The bath was then filled with Glycoline, and readings of the liquid volume were taken at various temperatures. In all cases care was taken to prevent condensation from occurring in the vicinity of the bend or on the surface of the mercury, by maintaining these parts at a slightly higher temperature, by means of the heating element mentioned above. The time allowed for the attainment of temperature and pressure equilibrium varied from 10 min. at lower temperatures to 30 min. when the temperature was within a few degrees of the critical. At the time of each reading, the position of the mercury on the horizontal scale was ascertained, so that the total volume was known.

When all the volume readings had been made, the bath liquid was removed and the dilatometer bulb cooled to -78° C. The whole apparatus was exhausted to a pressure less than 0.1 mm. and the mercury seals *I* and *J* were closed. The mercury in the U-tube was then allowed to warm to its melting point, and the leveling bulb *G* lowered, thus connecting the dilatometer with the body of the apparatus. The liquid was then completely distilled into the bulb *K*, which was cooled with liquid air. At this temperature the vapor pressure is negligible, as is the amount left in the vapor state. The bulb *K* was sealed off at the capillary neck. The amount of liquid could now be determined with great accuracy by weighing the bulb, first filled with liquid, then with dry air, and then with water to determine the correction for the weight of air. In breaking off the tip of the bulb to release the liquid, care was taken not to lose any bits of glass. In the case of propylene the bulbs had to stand pressures of 12-13 atm., but weighed only 7-9 gm.

The method of calculating the densities has been given in detail by Maass and Wright (4). The change in volume due to expansion of the glass with temperature was small, and the corrections for it were easily made. To determine the amount of substance in the vapor state and thus ascertain the true weight of liquid, it was necessary to know the vapor densities. Since, however, the dead space of vapor was in all cases relatively small, a large error in the vapor density value used would not affect the experimental accuracy, except at the highest temperatures, where a 1% error in vapor density would cause an error of about 0.1% in liquid density. The vapor densities used were those of Cardoso and Coppola (2), and Winkler and Maass (7). No data were available regarding the density of propylene vapor below 66° C. These were calculated with sufficient accuracy from the known values above 66° C. by means of Van der Waal's equation.

Experimental Results

The results are listed by runs in Tables I and II. In Tables III and IV these are again listed, along with those of other investigators, and the deviation of each from a smooth curve is given.

Runs No. 1 and 2, Table II (methyl ether), were made on individually prepared samples. In Table IV it will be seen that there is excellent agreement between the two. Very close agreement is also found between the values obtained by Maass and Wright (4), and Maass, Boomer and Morrison (3),

TABLE I
DENSITY OF LIQUID PROPYLENE

Run No. 1		Run No. 2	
Temp., °C.	Density, gm./cc.	Temp., °C.	Density, gm./cc.
20.1	.5166	82.15	.3573
27.2	.5030	83.4	.3510
32.5	.4933	85.6	.3384
37.9	.4832	87.0	.3265
43.5	.4721	88.2	.3160
49.85	.4582	88.55	.3133
55.4	.4456		
59.65	.4350		
64.4	.4222		

TABLE II
DENSITY OF LIQUID METHYL ETHER

Run No. 1		Run No. 2		Run No. 3		Run No. 4	
Temp., °C.	Density, gm./cc.	Temp., °C.	Density, gm./cc.	Temp., °C.	Density, gm./cc.	Temp., °C.	Density, gm./cc.
13.85	.6784	7.4	.6877	87.25	.5355	111.1	.4559
20.55	.6680	7.9	.6872	90.75	.5254	111.95	.4519
26.0	.6593	8.8	.6857	97.4	.5060	114.4	.4405
35.05	.6443	11.3	.6818	102.5	.4885	117.1	.4247
		12.4	.6805	107.6	.4696	120.05	.4048
		22.55	.6647				
		32.2	.6485				
		41.05	.6332				
		51.0	.6153				
		60.15	.5975				
		71.65	.5736				
		75.0	.5664				

TABLE III
 DENSITIES OF LIQUID PROPYLENE: -78 TO 90° C.

Author	Temp., $^{\circ}$ C.	Density, gm./cc.	Deviation from curve, parts/1000	Author	Temp., $^{\circ}$ C.	Density, gm./cc.	Deviation from curve, parts/1000
Maass and Wright (4)	-78.2	.6486	—	Pall and Maass	55.4	.4456	—
	-58.5	.6247	—		59.65	.4350	—
	-48.5	.6109	-2		64.4	.4222	—
	-37.45	.5973	—		82.15	.3573	-0.7
	-34.4	.5937	—		83.4	.3510	—
	-27.85	.5854	$+3$		85.6	.3384	$+3.5$
	-15.65	.5691	—		87.0	.3265	—
	0	.5473	—		88.2	.3160	-0.6
	19.0	.5183	—		88.55	.3133	$+0.6$
Pall and Maass	20.1	.5166	—	Winkler and Maass (7)	67.6	.4080	-12
	27.2	.5030	-1		72.5	.3937	-9
	32.5	.4933	—		77.6	.3770	-2
	37.9	.4832	—		82.7	.3540	—
	43.5	.4721	—		87.5	.3136	-30
	49.85	.4582	—		89.7	.2983	—
					90.7	.2776	—

 TABLE IV
 DENSITIES OF LIQUID METHYL ETHER: -40° TO 120° C.

Author	Temp., $^{\circ}$ C.	Density, gm./cc.	Deviation from curve, parts/1000	Author	Temp., $^{\circ}$ C.	Density, gm./cc.	Deviation from curve, parts/1000
Maass, Boomer and Mor- rison (3)	-40.5	.7565	—	Pall and Maass	41.05	.6332	—
	-39.7	.7557	$+0.5$		51.0	.6153	—
	-36.7	.7507	—		60.15	.5975	—
	-34.0	.7473	$+0.5$		71.65	.5736	—
	-32.5	.7447	—		75.0	.5664	$+0.5$
	-28.6	.7393	—		87.25	.5355	—
	-25.1	.7374	$+4.6$		90.75	.5254	-0.4
	-21.4	.7289	—		97.4	.5060	—
	-16.5	.7220	-0.7		102.5	.4885	-0.3
	-14.7	.7201	—		107.6	.4696	-0.5
	-11.5	.7154	—		111.1	.4559	—
					111.95	.4519	—
Pall and Maass	7.4	.6877	-0.3		114.4	.4405	$+1$
	7.9	.6872	—		117.1	.4247	—
	8.8	.6957	-0.3		120.05	.4048	—
	11.3	.6818	-0.3	Cordoso and Cop- pola (2)	0.2	.6903	-12
	12.4	.6805	—		29.85	.6458	-5
	13.85	.6784	—		56.05	.6012	-8
	20.55	.6680	—		80.15	.5522	-4
	22.55	.6647	—		96.52	.5042	-9
	26.0	.6593	—		110.5	.4550	-8
	32.2	.6485	—		115.9	.4308	-2
	35.05	.6443	$+0.6$				

and those established in the present investigation. Winkler and Maass (7) give densities for propylene which coincide over a considerable part of their range, but the end values seem to be in error. While the results of Cardoso and Coppola (2) differ considerably at lower temperatures, the two curves approach each other and appear to coincide at about 122° C.

In Tables V and VI the densities of propylene and methyl ether are given at regular temperature intervals over the range for which they are accurately known. The values for propylene between 64° and 83° C. were obtained by mathematical interpolation.

TABLE V
DENSITY OF LIQUID PROPYLENE AT REGULAR TEMPERATURE INTERVALS

Temp., °C.	Density, gm./cc.	Temp., °C.	Density, gm./cc.	Temp., °C.	Density, gm./cc.
-80	.6507	-10	.5614	60	.4341
-70	.6388	0	.5473	70	.4058
-60	.6266	10	.5329	75	.3885
-50	.6138	20	.5167	80	.3672
-40	.6008	30	.4982	85	.3412
-30	.5877	40	.4790	88	.3180
-20	.5749	50	.4578		

TABLE VI
DENSITY OF LIQUID METHYL ETHER AT REGULAR TEMPERATURE INTERVALS

Temp., °C.	Density, gm./cc.	Temp., °C.	Density, gm./cc.	Temp., °C.	Density, gm./cc.
-40	.7558	40	.6350	95	.5137
-30	.7416	50	.6171	100	.4978
-20	.7272	60	.5978	105	.4793
-10	.7131	70	.5772	110	.4607
0	.6988	75	.5661	115	.4369
10	.6840	80	.5546	120	.4051
20	.6689	85	.5420		
30	.6520	90	.5278		

Discussion of Results

The new type of apparatus proved to be satisfactory. Although it is a rather elaborate set-up, once built it can be used with great facility for the density determination of any liquid having a reasonably high vapor pressure at room temperature. Since the dilatometer itself is not removed and weighed, it can be filled a number of times and a large temperature range thus covered. In this way the volume occupied by the vapor is kept relatively small, and the error in estimating its weight is correspondingly unimportant, although the vapor density may have an uncertain value comparable in magnitude with the liquid density.

The maximum error in a single determination is 1 part in 2000, and is estimated to be half this when the values are taken from a smooth curve drawn through all the points. This is true except for that part of the range where the temperature gradient becomes large, and the accuracy is limited by the exactness of temperature measurement. An accuracy of only 1 part in 1000 can be claimed for the densities of propylene above 80° C. and methyl ether above 100° C. It was found that the determinations made by the writers

were in good agreement with the values given by two other investigators working at lower temperatures. Calculations are made below on the basis of the law of corresponding states; these indicate that the accuracy claimed is warranted.

Application of the law of corresponding states leads to the conclusion that if the densities of two liquids are determined at corresponding temperatures, the ratio of these densities should be a constant. This is strictly true only when the densities are determined at the same corresponding pressures. It is only at high pressures that the density is measurably influenced by this factor, and a calculation made using the vapor pressure data of Cardoso and Bruno (1), and Seibert and Burrell (5), showed that at corresponding temperatures the vapor pressures were at the same corresponding pressures.

Methyl ether was chosen as the reference liquid, as there is good agreement in the literature regarding its critical temperature, 126.9° C. For propylene, critical temperature values are found varying between 91.9° and 92.6° C. In Table VII the temperatures and densities of methyl ether are given in columns 1 and 2, and the corresponding temperatures in column 3. In columns 4, 7, 10, and 13 are the corresponding temperatures of propylene calculated on the basis of critical temperatures of 91.7°, 92.0°, 92.1° and 92.3° C. respectively. Each of these is followed by two columns giving the appertaining densities, and the ratio of the densities.

These results are best analyzed by means of the graphical representation in Fig. 2. In this figure the radius of each circle corresponds to 1 part in 2000. It is seen that in the case where 92.1° C. was chosen as the critical temperature of propylene (Fig. 2C), a horizontal line can be drawn which passes through all the circles except the last two. This indicates that up to within 7°

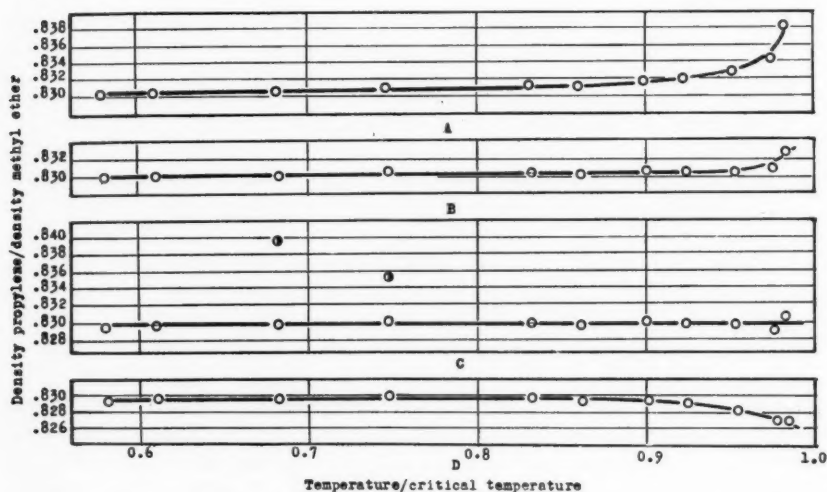


FIG. 2. Density ratio of propylene and methyl ether at corresponding temperatures.

of the critical temperature the densities of propylene and methyl ether as determined have values in agreement with the principle of the equation of corresponding states. Notice that an error of 1 part in 4000 in opposite directions in each density value would mean that the line would not pass through the circle representing such a point.

It is interesting to note how sensitive the constancy of the density ratio is to change in the critical temperature chosen. At 91.7°C . the ratio increases with rise in temperature, and there is a marked curvature upwards as the critical is approached (Fig. 2A). The reverse is true when 92.3°C . is taken as the critical temperature (Fig. 2D). In fact, an appreciable change in curvature seems to be caused by a 0.1° variation in the value of the critical temperature chosen. In Fig. 2C, this value is taken as 92.1°C ., which is in best agreement with the values experimentally determined in this laboratory, and in Fig 2B, 92.0°C . is used.

When the densities found by Cardoso and Coppola (2) for methyl ether are taken at 0° and 26.1°C . and the densities of propylene as given by Maass and Wright (4) calculated for the corresponding temperatures, the ratios found are respectively, 0.8397, and 0.8355. These are represented in Fig. 2C by the shaded circles. It is seen that they not only differ by a large amount from the value calculated on the data presented, but also disagree among themselves.

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THE SORPTION OF IODINE BY POLYVINYL ALCOHOL¹

BY WILFRED GALLAY²

Abstract

Iodine is taken up by polyvinyl alcohol from aqueous solution according to the adsorption isotherm. From aqueous methyl and ethyl alcohol solutions, the sorption obeys Henry's law. One electrolyte measured was absorbed by the colloid. The relation of Kroecker between weight of adsorbent and sorption of adsorbate, keeping total adsorbate constant, holds only at higher concentrations of adsorbent. Pre-absorption of an electrolyte does not materially affect adsorption of iodine by polyvinyl alcohol. The nature of the blue polyvinyl alcohol-iodine complex is discussed.

A number of substances other than starch have been shown to give a blue color with iodine. Among these may be mentioned pyrone and flavone derivatives (1), cholalic acid (6), euxanthic ester (4), lanthanum acetate (6), etc. The sorbents are in the colloidal state and a further class specificity is indicated. Polyvinyl alcohol also yields a blue color with iodine, a phenomenon briefly mentioned by Staudinger and co-workers (7) in connection with their studies on polyvinyl acetate and its hydrolysis.

Polyvinyl alcohol is readily obtained by either acid or alkaline hydrolysis from the corresponding acetate ester. According to the experimental conditions and to the degree of polymerization of the ester used, it is obtained in varying forms showing widely different degrees of polymerization. It may be readily freed from residual polyvinyl acetate by solution in water and precipitation by a non-solvent miscible with water, and finally freed from electrolytes by repeated dialysis. In the present instance, two polyvinyl alcohols were prepared, one from a low-polymerized ester and one from a high-polymerized ester. The solubility in water depends on the degree of polymerization, a 15% solution being readily obtained with the former (A), while a maximum solubility of about 3% only could be obtained with the latter (B). As is usual with this type of material, the viscosity-concentration relations of these two poly-alcohols showed wide differences (Fig. 1).

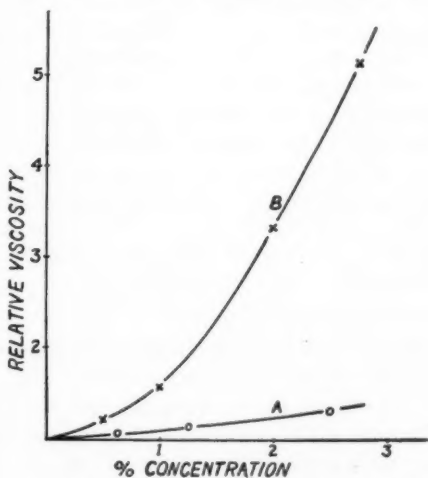


FIG. 1. Viscosity-concentration relation, Polymers A and B.

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The polyvinyl alcohol sol is typical of the hydrophilic sols which owe their great stability almost entirely to their power of solvation. Concentrated solutions of many inorganic salts precipitate the colloid owing to desolvating action. Non-solvents miscible with water have the same effect. Polyvinyl alcohol may be considered somewhat similar to starch in many respects. Both are polyhydroxy alcohols yielding sols similar in character. Both are polymers whose degree of polymerization can be readily changed by physical means. However, starch consists of carbohydrates whose similarity of structure is not certain, and a portion of the starch is bound in complexes with inorganic material. The purification of the natural product is difficult. Polyvinyl alcohol, on the other hand, is a synthetic polymer of a known unit, consisting of a mixture of polymers of varying molecular size but all of which are probably built up in the same manner. It was of particular interest, therefore, to note quantitatively the sorption of iodine by this synthetic carbohydrate.

When a polyvinyl alcohol sol is treated with an aqueous iodine solution of a concentration higher than a certain minimum, a deep blue color is produced. The blue color changes through bluish green, green, greenish-yellow to colorless on heating, and through the reverse order back to blue on cooling. It appears probable that these intermediate colors are mixtures of the blue of the complex and the yellow of the aqueous iodine solution. The more concentrated the solution, the longer is the period of heating necessary to bring about the disappearance of the color, and the more readily it reappears on cooling. The sensitivity of the reaction is much less than that with starch, a much larger quantity of iodine being necessary to produce the blue color with a sol of the polymer. When obtained, however, the sol may be diluted with only corresponding decrease in intensity of color. Substances such as sodium thiosulphate and sodium sulphite capable of reacting with iodine, destroy the blue color stoichiometrically, while excess of most other electrolytes results in the precipitation of the complex. The precipitated complex may be filtered and dried, whereupon it is obtained as a pulverizable powder, blue with a violet iridescence. This iridescence disappears on long exposure to the air. The solid redissolves readily in water with re-formation of the blue color. Solid polyvinyl alcohol takes up practically no iodine, the swollen or solvated condition being necessary for sorption.

Polyvinyl alcohol sols were treated with aqueous iodine solutions of varying concentrations, and measurements made of the amount of iodine left in solution after precipitating the complex. The results are expressed in Fig. 2. The curves have the character of the general adsorption isotherm, the logarithmic derivatives being shown in Fig. 3.

It is to be noted that these adsorption values represent only a fraction of the true values in the unprecipitated sol, since the solvation and therefore also the adsorption have been very greatly decreased by precipitation. This is shown also in the different values obtained with sodium chloride and mag-

nesium sulphate as precipitants. As shown in another instance (3), the character of the adsorption has also been changed, as indicated by the non-affine Curves 1 and 2 in Fig. 3.

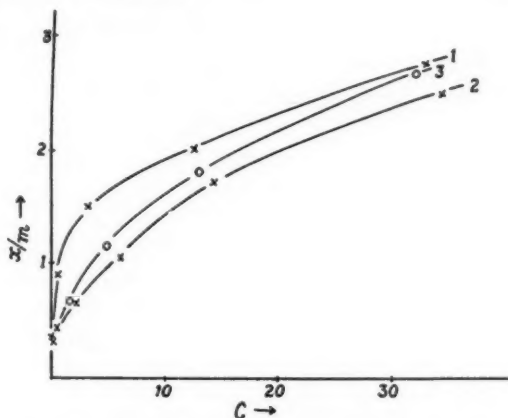


FIG. 2. Sorption of iodine by:—1. Polymer A (precipitant—sodium chloride); 2, Polymer A (precipitant—magnesium sulphate); 3, Polymer B (precipitant—sodium chloride).

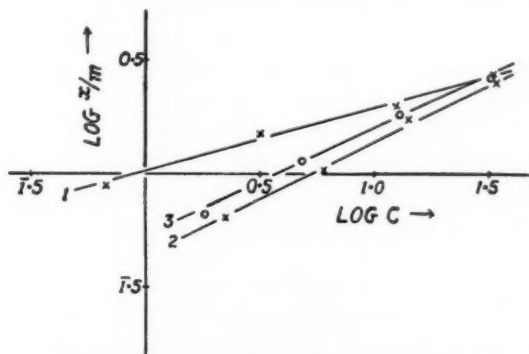


FIG. 3. Logarithmic derivatives of curves in Fig. 2.

Varying concentrations of polyvinyl alcohol were treated with a constant amount of iodine, keeping the total volume constant. The following relation has been proposed by Kroeker (5),

$$\lambda = \frac{v}{m} \log \frac{C_a}{C},$$

where v is the total volume, m the weight of the adsorbent, C_a the total concentration of adsorbate and C the concentration at equilibrium, and λ a constant. In Tables III and IV, values for λ with change in m and C have been calculated. It is seen that this relation holds only for higher values of m , values of λ increasing sharply for very dilute sols.

In further sorption measurements, non-aqueous precipitants were used and the equilibrium values of iodine in solution measured. The experiments were done with methyl alcohol at 0°, 22°, 35° C. and with ethyl alcohol at 22° C.

The results are shown in Fig 4.

The sorption is shown to be a partition of iodine between polymer and liquid according to Henry's law, with no evidence of adsorption. The writer has discussed a similar effect in another instance (3). It is apparent that the mutual attraction between iodine and the solvent has been so increased by the addition of methyl or ethyl alcohol that adsorption has been reduced to a minimum, leaving merely an absorption or solution of the iodine in the colloid. In

other words, the exponent in

the adsorption isotherm is changed in value to one and the expression becomes one of simple partition. From Fig. 4, also, may be seen the magnitude of the effect of temperature on this sorption. The temperature coefficient is negative.

Fig. 5 expresses the sorption of sodium bicarbonate by polyvinyl alcohol. Here also the effect is one of absorption rather than adsorption by the colloid.

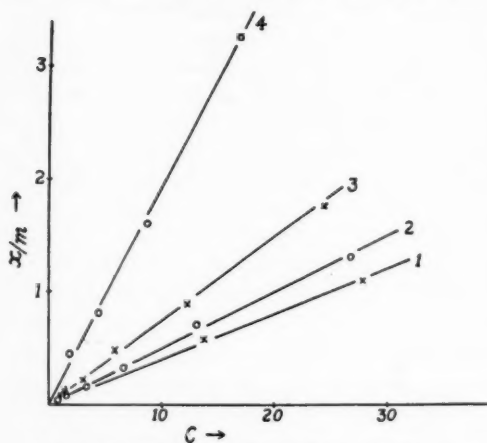


FIG. 4. Sorption of iodine on Polymer A, using non-aqueous precipitants—1, methyl alcohol at 35° C.; 2, methyl alcohol at 22° C.; 3, methyl alcohol at 0° C.; 4, ethyl alcohol at 22° C.

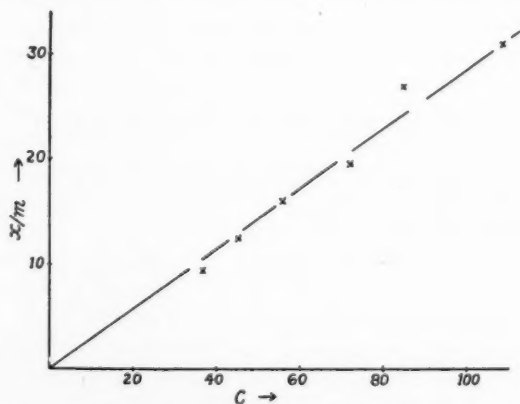


FIG. 5. Sorption of sodium bicarbonate on polyvinyl alcohol.

Experiments were carried out also (Table VIII) on the sorption of iodine by polyvinyl alcohol after the colloid had absorbed an electrolyte. The effect of pre-absorption in the cases of three electrolytes, using various concentrations, was found to be very small. The adsorption of iodine is not affected by materials absorbed by the colloid.

The effect of degree of polymerization on the extent of sorption is small as shown in these experiments, the adsorption decreasing somewhat with increased molecular weight of colloid.

With regard generally to those substances yielding a blue color with iodine, a general specificity is shown in that all these substances are in the colloidal state of subdivision. This is particularly well shown in the case of the acetates of the rare earths, where the blue color is obtained only during the transitory amorphous stage before crystallization begins. A lower limit of colloidal size is noted for this phenomenon with the low viscosity dextrans which may be considered as hemi-colloids. A further class specificity is noted also in constitution. It was at one time considered that the presence of conjugated double bonds was necessary for this reaction, but it was later shown that this did not hold in many instances. Bergmann (2) has put forth the view that the presence of an oxygen bridge in the molecule is necessary, and indeed most of the substances showing this blue color with iodine probably contain oxygen atoms heterocyclically bound. However in the case of polyvinyl alcohol, from its general reactions and from our knowledge of polymers of this type, it is certain that most of the oxygen is present as hydroxyl oxygen, so that the category of these substances giving a blue color with iodine must be enlarged, unless it is assumed that the polymer contains a number of inner ether linkages also. Polyvinyl alcohol would then belong to the class discussed by Bergmann. Whether labile hydrogen or other mode of polymerization is assumed, would make no difference. The possibility that iodine is present in the colloidal state protected by the polyvinyl alcohol is altogether unlikely. The disappearance of color with rise in temperature is reversible. This is not compatible generally with protective action. Substances such as polyvinyl alcohol and starch are comparatively poor protective agents. Furthermore, colloidal iodine, prepared by the plural protection method, has not been prepared with a blue color. Iodine absorbed or dissolved in the colloid does not give a blue color. The combination of adsorption and a specialized linkage in the colloid is apparently necessary for this phenomenon.

Experimental

The method recommended by Staudinger (7) was used for the preparation of polyvinyl alcohol. Two samples of polyvinyl acetate of widely different degrees of polymerization were used as initial materials. After complete hydrolysis with sodium methylate, the corresponding alcohols formed were dialyzed, precipitated by a non-solvent, dried and dialyzed again. After subsequent precipitation and drying *in vacuo*, a white cellulose-like material

was obtained as the low polymer, *A*, and a yellowish, rather brittle product as the high polymer, *B*. The polymers contained only traces of inorganic impurities.

All iodine-potassium iodide solutions were made up by diluting a standard stock solution, hence the ratio of iodine to potassium iodide was constant throughout.

Portions (5 cc.) of a 2.5% solution of *A* were treated with 2 cc. of aqueous iodine-potassium iodide solutions of varying concentrations of iodine. After thorough shaking and allowing to stand overnight, 13 cc. of saturated sodium chloride solution was added to each sol to precipitate the polymer-iodine complex. After shaking and allowing to stand for several hours, the suspension was centrifuged and the iodine in the supernatant liquid titrated with the sodium thiosulphate. The same procedure was carried out also with saturated magnesium sulphate solution as precipitant. The results are shown in Table I.

TABLE I
SORPTION OF IODINE BY POLYMER A

Total iodine, gm.	Iodine sorbed, gm.	<i>C</i>	<i>x/m</i>	Total iodine, gm.	Iodine sorbed, gm.	<i>C</i>	<i>x/m</i>
<i>a. Precipitant—saturated sodium chloride</i>				<i>b. Precipitant—saturated magnesium sulphate</i>			
0.0114	0.0114	0	0.36	0.0114	0.0101	0.26	0.32
0.0162	0.0136	0.51	0.43	0.0162	0.0136	0.51	0.43
0.0320	0.0286	0.67	0.90	0.0320	0.0206	2.25	0.65
0.0635	0.0475	3.15	1.50	0.0635	0.0330	6.01	1.04
0.1271	0.0637	12.49	2.01	0.1271	0.0548	14.24	1.73
0.2538	0.0875	32.76	2.76	0.2538	0.0799	34.26	2.52

NOTE:—*C* = millimoles of iodine per litre in solution at equilibrium. *x/m* = millimoles of iodine sorbed per gram of polymer.

Portions (5 cc.) of a 2.67% solution of Polymer *B* were treated with iodine as described above, using saturated sodium chloride as precipitant.

TABLE II
SORPTION OF IODINE BY POLYMER B

Total iodine, gm.	Iodine sorbed, gm.	<i>C</i>	<i>x/m</i>
0.0317	0.0225	1.81	0.66
0.0635	0.0388	4.87	1.15
0.1269	0.0617	12.84	1.82
0.2538	0.0910	32.07	2.69

Tables III and IV show the sorption of iodine per gram of polymer when the concentration of the latter is varied, the total volume of solution being kept constant. The concentrations used are those denoted by m gm. per standard volume (30 cc.). Saturated sodium chloride was used as precipitant in all cases.

TABLE III
SORPTION OF IODINE WITH CHANGE IN CONCENTRATION OF A
Total iodine in each case, 0.1896 gm.

Iodine sorbed, gm.	M , gm.	C	x/m	$\lambda = \frac{v}{m} \log \frac{C_a}{C}$
0.0159	0.0125	27.38	5.01	90.7
0.0254	0.0250	25.88	4.00	75.1
0.0380	0.0500	23.89	2.99	58.2
0.0420	0.0750	23.26	2.21	43.6
0.0555	0.1000	21.13	2.19	45.2
0.0777	0.1500	17.64	2.04	45.8
0.0888	0.2000	15.89	1.75	41.2
0.1046	0.2500	13.40	1.65	41.8
0.1173	0.3000	11.40	1.54	41.9

TABLE IV
SORPTION OF IODINE WITH CHANGE IN CONCENTRATION OF B
Total iodine in each case, 0.1894 gm.

Iodine sorbed, gm.	M , gm.	C	x/m	$\lambda = \frac{v}{m} \log \frac{C_a}{C}$
0.0328	0.0175	24.68	7.38	142.3
0.0418	0.0350	23.26	4.7	111.1
0.0552	0.0700	21.15	3.11	63.8
0.0808	0.1400	17.12	2.27	51.6

The viscosities of solutions of Polymers A and B were measured in an Ostwald viscosimeter, and expressed relative to the viscosity of water at the same temperature.

TABLE V
VISCOSITIES OF POLYMERS A AND B

Polymer A		Polymer B	
% Conc.	Rel. visc.	% Conc.	Rel. visc.
0.625	1.07	0.5	1.21
1.25	1.14	1.0	1.56
2.50	1.31	2.0	3.34
		2.75	5.17

The sorption of iodine by Polymer A was then measured, using non-aqueous precipitants. Table VI shows the results obtained with methyl alcohol at three different temperatures and ethyl alcohol at one temperature. The general procedure was the same as that previously described, and equilibrium was attained in each case at the temperature indicated.

TABLE VI
SORPTION OF IODINE ON POLYMER A, USING NON-AQUEOUS PRECIPITANTS

Total iodine, gm.	Iodine sorbed, gm.	C	x/m
<i>a. Precipitant—methyl alcohol Temp., 0° C.</i>			
0.0114	0.0032	1.08	0.08
0.0162	0.0045	1.54	0.12
0.0320	0.0084	3.10	0.22
0.0635	0.0182	5.95	0.48
0.1271	0.0332	12.33	0.87
0.2538	0.0670	24.53	1.76
<i>b. Precipitant—methyl alcohol Temp., 22° C.</i>			
0.0079	0.0011	0.89	0.03
0.0159	0.0025	1.76	0.07
0.0317	0.0058	3.40	0.15
0.0635	0.0121	6.75	0.32
0.1269	0.0268	13.15	0.70
0.2538	0.0493	26.86	1.30
<i>c. Precipitant—methyl alcohol Temp., 35° C.</i>			
0.1271	0.0220	13.80	0.58
0.2538	0.0413	27.91	1.09
<i>d. Precipitant—ethyl alcohol Temp., 22° C.</i>			
0.0317	0.0175	1.86	0.46
0.0635	0.0301	4.39	0.81
0.1269	0.0611	8.64	1.61
0.2538	0.1245	16.98	3.27

Table VII shows the sorption of sodium bicarbonate by Polymer A. In each case to 5 cc. of a 2.5% solution of the polymer there were added varying amounts of sodium bicarbonate in solution, and the complex after standing was precipitated by saturated sodium chloride. The sodium bicarbonate in solution at equilibrium was titrated after centrifuging.

TABLE VII
SORPTION OF SODIUM BICARBONATE BY POLYMER A

Total sodium bicarbonate, gm.	Sodium bicarbonate sorbed, gm.	C	x/m
0.1764	0.0991	36.8	9.44
0.2266	0.1317	45.2	12.54
0.2856	0.1680	56.0	16.00
0.3570	0.2058	72.0	19.60
0.4620	0.2839	84.8	27.04
0.5544	0.3259	108.8	31.03

Table VIII shows the effect of pretreatment with several inorganic salts on the subsequent sorption of iodine by the polymer. In each case 5 cc. of a 2.8% solution of Polymer A was allowed to stand for several hours with 5 cc. of varying concentrations of the salt, after which 2 cc. of 0.5 *N* iodine solution was added. After equilibrium was attained, the volume in each case was made up to 20 cc. with saturated sodium chloride. The iodine in solution was determined after centrifuging.

TABLE VIII
SORPTION OF IODINE BY POLYMER A AFTER PRETREATMENT
Total iodine in each case, 0.1271 gm.

Salt added, millimoles/litre	Iodine sorbed, gm.	<i>C</i>	<i>x/m</i>
<i>a. Effect of sodium bicarbonate</i>			
0	0.0704	11.17	1.98
105	0.0739	10.48	2.08
135	0.0751	10.24	2.11
170	0.0748	10.30	2.11
213	0.0745	10.36	2.10
275	0.0739	10.48	2.08
330	0.0739	10.48	2.08
<i>b. Effect of magnesium sulphate</i>			
0	0.0713	10.99	2.01
15.2	0.0700	11.25	1.97
30.4	0.0694	11.37	1.95
60.9	0.0694	11.37	1.95
121.7	0.0707	11.11	1.99
243.4	0.0700	11.25	1.97
304.3	0.0691	11.42	1.94
<i>c. Effect of potassium iodide</i>			
0	0.0710	11.05	2.00
37.7	0.0719	10.88	2.02
75.3	0.0723	10.80	2.03
150.6	0.0721	10.84	2.03
301.2	0.0719	10.88	2.02

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